ZEBRA MUSSEL ADHESION AND ASPECTS OF ITS PREVENTION USING COPPER

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
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Abstract

The development of non-chemical control strategies for zebra mussel biofouling requires a more complete understanding of zebra mussel attachment. A wall-jet apparatus was designed to measure one aspect of attachment; the strength with which zebra mussels bind to substrates. The results indicate a significant difference in adhesion strength among the materials, ranging in mean values from $0.002 \pm 0.0002 \text{ Pa m}^2$ for smooth Teflon to $0.012 \pm 0.0005 \text{ Pa m}^2$ for medium roughness mild steel. The adhesion strength increased with roughness for Teflon and stainless steel.

A tensile load test was also used to evaluate the adhesion strength of zebra mussel to materials. The results obtained from this method were comparable to the wall-jet data, and indicated a difference in adhesion strength among materials with mean detachment force values ranging from $0.183 \pm 0.037 \text{ N}$ for smooth Teflon to $1.606 \pm 0.162 \text{ N}$ for smooth mild steel.

Another aspect of zebra mussel attachment is the prevention of recruitment onto a surface. Recent recruitment studies have shown that zebra mussels do not attach to copper surfaces. In order to better understand the anti-fouling mechanisms of copper, release rates and surface characteristics of various copper-containing materials were compared.

Copper and nickel release rate studies were performed under both batch and continuous-flow conditions. Under batch conditions, the copper concentration within the vessel increased to a level which influenced the copper release rate and therefore, continuous-flow conditions are preferred. The results from the continuous-flow studies showed that as the copper content of the copper-nickel alloy increased both the copper and nickel release rates increased. The release rate of copper and nickel from acid-etched plates of Cu:Ni 90:10 were 27.7 mg m$^{-2}$ day$^{-1}$ and
5.2 mg m\(^{-2}\) day\(^{-1}\), from Cu:Ni 80:20 were 5.3 mg m\(^{-2}\) day\(^{-1}\) and 1.5 mg m\(^{-2}\) day\(^{-1}\), and from Cu:Ni 70:30 were 1.8 mg m\(^{-2}\) day\(^{-1}\) and 0.8 mg m\(^{-2}\) day\(^{-1}\), respectively. The release of copper and nickel from copper and copper-nickel alloys can be described using a comprehensive model which described the initial dissolution process under continuous-flow conditions as being controlled by reaction-limited conditions.

A comparison of the characteristics of copper-based materials and their anti-fouling performance indicated that the copper release rate correlated with the prevention of zebra mussel attachment. Suppressing the copper release rate and examining the surface characteristics of those materials confirmed that copper release prevents zebra mussel attachment.
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TABLE OF CONTENTS

1.0 Introduction ........................................................................................................... 1
1.1 Background ........................................................................................................... 1
1.2 Objectives ............................................................................................................. 3
1.3 Outline of Thesis ................................................................................................... 3

2.0 Literature Review and Theoretical Background .................................................... 5
2.1 Zebra Mussel Adhesion Strength Studies ............................................................... 5
2.2 Fluid Mechanics Relating to the Wall-Jet .............................................................. 6
2.3 Characteristics of Copper .................................................................................... 13
    2.3.1 Bio fouling Resistance and Copper Toxicity ................................................. 13
    2.3.2 Corrosion of Copper ..................................................................................... 16
    2.3.3 Copper Release Rates .................................................................................... 19
        2.3.3.1 Water Chemistry and Conditions ......................................................... 20
        2.3.3.2 Experimental Techniques ................................................................... 22

3.0 Zebra Mussel Adhesion Strength Studies ............................................................. 29
3.1 Introduction ............................................................................................................ 29
3.2 Materials and Methods ......................................................................................... 31
    3.2.1 Wall Jet Adhesion Strength Measuring System ............................................. 31
    3.2.2 Experimental Procedure .............................................................................. 33
3.3 Results .................................................................................................................... 37
    3.3.1 Wall Jet Fluid Flow Characteristics ............................................................. 37
    3.3.2 Adhesion Strength of Zebra Mussels .......................................................... 39
    3.3.3 Statistical Analysis .................................................................................... 44
3.4 Discussion ............................................................................................................... 46
    3.4.1 Wall Jet Characterization ............................................................................ 46
    3.4.2 Attachment Strength of Zebra Mussels ....................................................... 50
    3.4.3 Adhesion Strength Theory .......................................................................... 54
3.5 Conclusions ........................................................................................................... 55

4.0 Measurements and Modeling of Copper Release Rates in Lake Water ................. 58
4.1 Introduction ........................................................................................................... 58
4.2 Methods and Materials ......................................................................................... 60
    4.2.1 Copper Release Rate Studies .................................................................... 60
        4.2.1.1 Batch Experiments ............................................................................. 60
        4.2.1.2 Continuous-Flow Experiments ............................................................ 68
4.3 Results .................................................................................................................... 71
    4.3.1 Batch Experiments ..................................................................................... 71
    4.3.2 Continuous-Flow Experiments .................................................................... 77
4.4 Copper Release Rate Model .................................................................................. 84
    4.4.1 Batch Release Rate Model ......................................................................... 88
    4.4.2 Continuous-Flow Release Rate Model ....................................................... 89
4.5 Discussion ................................................................. 92
  4.5.1 Batch Experimental Profiles ................................ 92
  4.5.2 Batch Model Parameters .................................... 99
  4.5.3 Continuous-Flow Experimental Profiles ............... 102
  4.5.4 Continuous-Flow Model Parameters .................. 105
4.6 Conclusions .......................................................... 110

5.0 Copper and Nickel Dissolution Rates from Copper-Nickel Alloys in Fresh
  Water ........................................................................ 113
  5.1 Introduction .......................................................... 113
    5.1.1 Copper Release Rate Model ............................... 114
  5.2 Methods and Materials .......................................... 115
    5.2.1 Copper and Nickel Release Rate Experiments ........ 115
      5.2.1.1 Batch Experiments .................................. 115
      5.2.1.2 Double-Exposure Experiment ..................... 117
      5.2.1.3 Continuous-Flow Experiments .................... 117
    5.2.2 Linear Polarization Measurements ................. 118
  5.3 Results ............................................................... 120
    5.3.1 Copper and Nickel Release Rate Experiments ........ 120
      5.3.1.1 Batch Experiments .................................. 120
      5.3.1.2 Continuous-Flow Experiments .................... 125
    5.3.2 Linear Polarization Measurements ................ 131
  5.4 Discussion .......................................................... 137
  5.5 Summary ............................................................ 150

6.0 Understanding the Anti-fouling Mechanism of Copper-Containing Materials. 152
  6.1 Introduction ........................................................ 152
  6.2 Methods and Materials .......................................... 153
    6.2.1 Lake Erie Conditioned Copper Alloys ............... 153
      6.2.1.1 X-ray Photoelectron Spectroscopy (XPS) Studies 154
      6.2.1.2 X-ray Diffraction Studies .......................... 155
      6.2.1.3 Scanning Electron Microscopy (SEM) Examination 155
      6.2.1.4 Release Rate Studies ................................ 155
    6.2.2 Galvanic Couple Experiments ....................... 157
    6.2.3 Copper Release Rate from Copper-Epoxy .......... 159
  6.3 Results ............................................................... 160
    6.3.1 Lake Water Conditioned Plates ...................... 160
      6.3.1.1 Surface Studies .................................... 160
      6.3.1.2 Copper Release Rates ............................. 163
    6.3.2 Galvanic Couples ......................................... 164
    6.3.3 Copper-Epoxy Release Rate ......................... 169
  6.4 Discussion .......................................................... 171
  6.5 Summary ............................................................ 177

7.0 Summary .............................................................. 179
8.0 Conclusions and Recommendations for Future Work ........................................ 184
  8.1 Conclusions ........................................................................................................ 184
  8.2 Recommendations for Future Work ................................................................. 186
9.0 Nomenclature ...................................................................................................... 187
10.0 References ......................................................................................................... 189

List of Figures

Figure 2.1: Wall-Jet Apparatus .................................................................................. 7
Figure 2.2: Pourbaix Diagram for the Copper-Water System .................................... 18
Figure 3.1: Wall Shear Stress Contours ................................................................. 38
Figure 3.2: Mean Fluid Detachment Parameter (DP) Results .................................. 43
Figure 3.3: Mean Detachment Force (DF) Results ................................................. 43
Figure 3.4: Correlation Between the Results from the Two Adhesion Strength
  Test Methods ......................................................................................................... 51
Figure 4.1: Experimental Set-up for Batch and Continuous-Flow Conditions ........... 62
Figure 4.2: Release Curve from Copper Batch Experiment ....................................... 72
Figure 4.3: Release Curves from Double Exposure Experiment .............................. 73
Figure 4.4: Release Curves from Second Double Exposure Experiment .................. 74
Figure 4.5: Continuum of Release Rate Curves ....................................................... 76
Figure 4.6: Long-term Batch Experimental Results ............................................... 78
Figure 4.7: Change in Copper Concentration under Continuous-Flow Conditions ... 79
Figure 4.8: Evaluation of Mass Transfer Effects on the Release of Copper ............... 82
Figure 4.9: Evaluation of Mass Transfer Effects on the Release of Copper ............... 83
Figure 4.10: Simplified View of Processes Occurring at the Copper Surface .......... 87
Figure 4.11: Batch-conditions Model ...................................................................... 101
Figure 4.12: Copper Release Rate as a Function of Flow Rate ................................ 108
Figure 5.1: Phase Diagram for Copper-Nickel Alloys ............................................ 122
Figure 5.2a: Copper Concentration Results from Batch Experiments
  using Copper-Nickel Alloys ............................................................................... 123
Figure 5.2b: Nickel Concentration Results from Batch Experiments
  using Copper-Nickel Alloys .............................................................................. 124
Figure 5.3: Double Exposure Experiments using Cu:Ni 80:20 .................................. 126
Figure 5.4a: Copper Release Rate for Cu:Ni 90:10 ................................................. 127
Figure 5.4b: Copper Release Rate for Cu:Ni 80:20 ................................................. 128
Figure 5.4c: Copper Release Rate for Cu:Ni 70:30 ................................................ 129
Figure 5.5: Effect of Conditioning Time Prior to Testing ........................................ 130
Figure 5.6a: Nickel Release Rate for Cu:Ni 90:10 ................................................... 133
Figure 5.6b: Nickel Release Rate for Cu:Ni 80:20 ................................................... 134
Figure 5.6c: Nickel Release Rate for Cu:Ni 70:30 ................................................... 135
Figure 5.7: Results from Linear Polarization Studies .............................................. 136
Figure 5.8: Results from Linear Polarization Studies using Lake Conditioned Coupons. 138
Figure 6.1: Schematic Diagram of the Continuous-Flow Vessel for Galvanic Couple Experiment ................................................. 158
Figure 6.2: SEM Photos of Lake Water Conditioned Coupons ................................................................. 162
Figure 6.3: Effects of Glutaraldehyde Treatment on Acid-Etched Coupons ................................................. 166
Figure 6.4: Comparison of Copper Release Rates from Lake Conditioned Coupons ............................................. 167
Figure 6.5: Comparison of Copper Release Rates from Lake Water Conditioned Coupons ................................. 168
Figure 6.6: Copper Release Rates from Copper Epoxy ................................................................................. 170

List of Tables

Table 3.1a: Materials, Surface Preparation and Surface Roughness of Test Plates used in this Work ................................................................. 34
Table 3.1b: Fluid Detachment Parameter (DP) of Zebra Mussels on Natural, Polymeric and Metallic Materials of Differing Surface Roughness .......... 40
Table 3.1c: Detachment Force (DF) of Zebra Mussels on Natural, Polymeric and Metallic Materials of Differing Surface Roughness .......................... 42
Table 3.2: Analysis of Variance of Mean Detachment Parameter .............................................................................. 45
Table 3.3: Analysis of Variance for Detachment Parameter ...................................................................................... 45
Table 3.4: Analysis of Variance of Mean Tensile Force ......................................................................................... 47
Table 3.5: Analysis of Variance for Detachment Force ......................................................................................... 48
Table 3.6: Comparison of Fluid Detachment Parameter and Tensile Force .............................................................. 51
Table 4.1: Description of Copper Batch Experiments ......................................................................................... 64
Table 4.2: Comparison between Lake Erie Water and Lake Ontario Water ........................................................ 67
Table 4.3: Description of Copper Continuous-Flow Experiments ........................................................................... 69
Table 5.1: Compositions of the Copper-Nickel Alloys used in this Study .................................................................... 117
Table 5.2: Comparison of Copper and Nickel Release Rates from Continuous-Flow Experiments ............................................................. 142
Table 5.3: Copper Release Rate Data ........................................................................................................... 144
Table 5.4: Comparison of Results from Linear Polarization Measurements ......................................................... 147
Table 5.5: Zebra Mussel Biofouling on Copper Materials ....................................................................................... 149
Table 6.1a: Elemental Species from XPS Survey of Lake Water Conditioned Plates ........................................... 161
Table 6.1b: XPS Results of Oxide Species on the Surfaces of the Conditioned Copper Plates ......................................................... 161
Table 6.2: Results from GFAAS Analysis of the Bulk Water from the Galvanic Couple Experiment .............................. 164
Table 6.3: XPS Results for the Oxide Species Present on Copper Plates from Galvanic Couples ......................................................... 169

APPENDIX A: Relationship between wall shear stress and detachment force .............................................. A1
APPENDIX B: Literature Review ............................................................................................................... B1
APPENDIX C: XPS Analytical Method ........................................................................................................... C1
Chapter 1

Introduction

1.1 Background

The zebra mussel, Dreissena polymorpha, is native to the Black and Caspian Seas (Resche, 1990), but now is found throughout Europe in freshwater bodies. It is believed to have been introduced into North America via ballast water discharged from ships originating from European ports. Since its first sightings in Lake St. Clair in June, 1988 (Ontario Ministry of Natural Resources, 1990), the zebra mussel has had detrimental ecological and economic impacts upon the Great Lakes. There have also been some positive effects since the introduction of the zebra mussel. For example, the water quality of Lake Erie has improved due to the high filtering rate of the large population of zebra mussels in the area.

Some of these impacts result from its unique characteristic of attachment by means of a byssal apparatus. The byssus allows zebra mussels to attach to any hard surface (Mackie, 1993), unlike native clams that settle onto the bottom sediment of lakes. The greatest engineering consequence of this behaviour has been the biofouling of water intakes causing pressure losses, reduction of pipe diameter, obstruction of valves and obnoxious odours from the death of mussels (O'Neill, 1988). Zebra mussel biofouling causes reduced productivity resulting from the increased operation down-time required to clean piping systems, and is expected to result in significant economic losses (Armor and Wiancko, 1993).

The control of zebra mussels contributes to the costs associated with their impacts. For example, physical removal of zebra mussels from water intake pipes is one method, although it is very costly and labour intensive. Chemical control strategies, such as chlorine
(sodium hypochlorite) flushing, are also costly and may be harmful to the natural aquatic environment. Therefore, new control strategies are needed to deal with the increasing problem of zebra mussel biofouling.

In order to develop alternate control strategies, a more complete understanding of zebra mussel attachment is necessary. In this work, two aspects of attachment are considered. The first is the strength with which a mussel binds to a surface. The second aspect is the prevention of attachment to surfaces.

Copper was selected as the principal material to be studied for preventing zebra mussel recruitment. The use of copper for the prevention of biofouling would alleviate some of the detrimental effects resulting from the introduction of zebra mussels into the Great Lakes. However, the potential impact on the aquatic environment resulting from the use of copper must be assessed, beginning with the quantification of copper leaching. As well, a better understanding of the mechanism by which copper prevents zebra mussel biofouling could be used in developing new materials for zebra mussel control.

The following work investigated the attachment strength of zebra mussels to various substrates, and studied the characteristics of copper-based materials that prevent mussel biofouling. The information gathered through this thesis work will aid in the development of new mitigation strategies that do not rely on adverse chemical treatment of the lake water environment.
1.2 Objectives

There were five objectives in this thesis research:

1. To develop a methodology to measure the adhesion strength of zebra mussels using a newly-designed wall-jet adhesion strength apparatus.

2. To use the wall-jet and direct mechanical pull-off techniques to measure the detachment strength of zebra mussels as a function of material type and roughness.

3. To identify the physical and chemical characteristics of copper and copper-nickel alloys that give rise to biofouling resistance.

4. To quantify the release rates of copper and nickel from copper and copper-nickel alloys in fresh water.

5. To develop a model to predict the rate of copper release from copper and copper-nickel alloys into fresh water.

Objectives 1 and 2 deal with the attachment strength of mussels which have established themselves on a surface. Objectives 3 to 5 pertain to the use of copper-containing surfaces to prevent zebra mussel biofouling.

1.3 Outline of Thesis

The thesis is divided into eight chapters. Chapter 2 is a review of the relevant literature and provides a theoretical background for the thesis. Chapter 3 summarizes the work completed to determine the adhesion strength of zebra mussels to various materials. This chapter is a combination of two papers previously published: "A wall-jet to measure the attachment strength in zebra mussels."; and "Attachment strength of zebra mussels on
natural, polymeric, and metallic materials." Chapters 4 and 5 represent the measurement and modeling of copper release rates from copper and copper-nickel alloys. Chapter 6 examines the mechanisms by which copper-containing materials prevent zebra mussel biofouling. Release rate results from Chapters 4, 5 and 6 have been incorporated into a paper which is currently under review by the Journal of Environmental Engineering. Chapter 7 is an overall summary and, Chapter 8 presents the conclusions of the thesis and lists recommendations for future work.
Chapter 2

Literature Review and Theoretical Background

2.1 Zebra Mussel Adhesion Strength Studies

There is very little information available concerning the adhesion strength of zebra mussels. The only investigation, to date, has been the work by Ackerman et al. (1992, 1993b), who describe the adhesion strength testing of zebra mussels to various substrates using a Rotating Disk Test System (RDTS). The four materials tested in those experiments were polyvinylchloride (PVC), polymethylmethacrylate (PMMA), stainless steel (SS), and aluminum (AL). The shear stress required to remove 95% of the mussels was 62 ± 5 Pa on PVC, 50 ± 3 Pa on PMMA, 48 ± 4 Pa on SS, and 31 ± 1 Pa on AL. The results indicated that there was a significant difference in adhesion strength among the substrates tested.

There is some information available that describes adhesion strength studies of marine invertebrates. The experiments by Young and Crisp (1982) used an adhesive testing device (strain gauge) to test the adhesion strength of the marine blue mussel, *Mytilus edulis* L.. A thread was glued onto the mussel and the gauge was pulled until the mussel was removed. The materials tested were slate, glass, paraffin wax and teflon, and the results indicated a significant difference in adhesion strength among the materials. The protein-based adhesive which comprises most of the byssal apparatus was expected to bond well to high energy polar surfaces but bond weakly to non-polar surfaces, as was indicated by the tests conducted.

Adhesion strength studies performed using the larvae (cyprids) of the barnacle *Balanus balanoides* used a piece of nichrome wire glued to the cyprid (Yule and Crisp,
The tensile load measurement, a force applied perpendicular to the surface, was used to test the adhesion strength of the cyprids to differently conditioned surfaces.

The majority of adhesion strength studies involve a form of direct mechanical testing. The wall-jet apparatus is another device for measuring adhesion strength; it has several advantages over the direct method techniques. The wall-jet is capable of performing adhesion strength testing on small zebra mussels which cannot be tested using the tensile load test method because they are too small and are crushed by the clamping device. Organisms that cannot be gripped by the tensile load clamping device, due to their irregular shapes, can be tested in the wall-jet. The wall-jet allows for the observation of the removal of a mussel exposed to natural flows and the events of detachment can be recorded using video microscopy. In addition, the adhesion strength results from the wall-jet apparatus can be used for direct application to cleaning procedures which use high pressure water-jet systems for the removal of zebra mussels in pipes.

2.2 Fluid Mechanics Relating to the Wall-Jet

In this study, a newly-designed wall-jet device (Figure 2.1) utilizing a flow of water impinging upon an object, is used to infer the attachment strength of zebra mussels to various substrates. The term wall-jet describes a flow from a nozzle flush with a solid surface discharging into surroundings of similar composition (Sigalla, 1958). The flow on the surface of the solid results in a shear stress across the surface.

One method for estimating the shear stress on the surface onto which the flow impinges is to assume that near the duct exit the shear stress value is the same as that at the
Figure 2.1: Wall-Jet Apparatus. (A) Scale drawing of the Wall-Jet Apparatus used to measure the adhesion strength of zebra mussels and (B) Details of the duct and chamber.
wall of the duct producing the flow. The shear stress is calculated by first determining the friction factor. For turbulent flow situations, the D'Arcy friction factor may be calculated using the relationship, (White, 1986),

\[
f = (1.8 \log\left(\frac{Re}{6.9}\right))^{(2)}
\]

where \(Re\) is the Reynolds number for turbulent pipe flow. The friction factor can be related to the wall shear stress for flow in a duct as follows (Jones, 1976):

\[
f = \frac{2D\left(\frac{dp}{dz}\right)}{\rho V^2}
\]

(2.2)

where \(\rho\) is the density of the fluid (kg\(m^3\)), \(V\) is the velocity of the flow (m\(s^{-1}\)), \(dp/dz\) is the pressure gradient for the flow (kg\(m^{-2}s^{-2}\)) and \(D\) is the diameter defined as:

\[
D = \frac{4A}{P}
\]

(2.3)

\[
\frac{dp}{dz} = \frac{f\rho V^2}{2D} = \frac{f\rho V^2 P}{8A}
\]

(2.4)

where \(A\) is the area of the duct opening (m\(^2\)) and \(P\) is the perimeter of the duct (m).
Rearranging Equation (2.2), results in

\[ \frac{dp}{dz} = \tau_w \frac{P}{A} \]  

(2.5)

where \( \tau_w \) is the wall shear stress. Therefore,

\[ \tau_w = \frac{f \rho V^2}{8} \]  

(2.6)

Equation (2.6) represents the wall shear stress for the flow through the wall-jet duct.

An alternate method to determine the wall shear stress at the surface onto which the flow impinges involves direct measurement of the shear stress using a Preston-static tube. The results from the work by Ackerman et al. (1993b) indicate that the Preston-static tube provides a reasonably accurate method to measure the wall shear stress. The tube consists of a static tap and a total pressure tap, both of which are used in the calculation of shear stress.

The shear stress is determined using a correlation between the non-dimensional shear stress, \( Y' \) (Equation 2.7), and the non-dimensional pressure difference, \( X' \) (Equation 2.8):

\[ Y' = \log_{10} \left( \frac{\tau_w d^2}{4 \rho V^2} \right) \]  

(2.7)
where $\tau_w$ is the wall shear stress (kg·m$^{-1}$·s$^{-2}$), $d$ is the outer diameter of the Preston tube (m), $\rho$ is the density of the fluid (kg·m$^{-3}$), $\nu$ is the kinematic viscosity of the fluid (m$^2$·s$^{-1}$). The non-dimensional pressure difference is given by:

$$X^* = \log_{10}(\frac{\Delta p}{4 \rho \nu^2})$$

(2.8)

where $\Delta p$ is the difference between the total pressure and static pressure (kg·m$^{-1}$·s$^{-2}$). The best relationship linking the two non-dimensional quantities is the linear equation proposed by Preston (1954),

This relationship was found to be the simplest and most amenable to the statistical analysis done in the experimentation by Ackerman et al. (1993b).

One of the key assumptions in the use of the wall-jet was that the wall shear stress at the point of mussel detachment, determined in the absence of the mussel, is directly related to the attachment strength of the mussel. Therefore, a relationship between the forces (lift and drag) acting on the mussel and the wall shear stress must be found in order to use this system to infer an attachment strength. Modeling done by Wiberg and Smith (1985) to determine the forces acting on sediment grains, indicated that both the drag force and the lift force were
proportional to the nominal wall shear stress. The sum of these forces, or the total force acting on the particle, is therefore, also proportional to the shear stress.

Using the relationships for the drag \( F_D \) and lift \( F_L \) forces,

\[
F_D = C_D \rho \frac{u_0^2}{2} A_D
\]  

(2.10)

where \( C_D \) is the drag coefficient, \( u_0 \) is the average velocity, and \( A_D \) is the projected area for the drag force, and

\[
F_L = \frac{\rho}{2} A_L C_L \left[ (u_0^2)_T - (u_0^2)_B \right]
\]  

(2.11)

where \( C_L \) is the lift coefficient, \( (u_0)_T \) and \( (u_0)_B \) are the average velocities at the top and bottom of the particle, respectively, and \( A_L \) is the projected area for the lift force. Wiberg and Smith concluded that the lift and drag forces are proportional to the local fluid velocities as shown by:

\[
F_D \propto u_0^2, \quad F_L \propto \left[ (u_0^2)_T - (u_0^2)_B \right]
\]  

(2.12)

It was also found that (Appendix A):

\[
u_o \propto \dot{u}^*
\]  

(2.13)
where \( u^* = \sqrt{\tau_w/\rho} \) is the kinematic velocity, therefore,

\[
(u^*)^2 \propto \tau_o \propto F_D \quad , \quad (u^*)^2 \propto \tau_o \propto F_L
\]  

(2.14)

This result indicates that the wall shear stress \( \tau_w \) is proportional to both the lift and drag forces acting on the mussel. Therefore, the total force acting on the mussel, the sum of the lift and drag forces, is also proportional to the wall shear stress \( \tau_w \). This relationship, by Wiberg and Smith, is valid only for a given size mussel. In determining the detachment parameter for zebra mussel adhesion, the square of the size of the mussel is multiplied by the wall shear stress in order to account for variability in mussel size. The length of the mussel was chosen to represent its size because there are uncertainties encountered in calculating the area of the mussels (i.e., irregular shape of the mussels, which area of the mussel to use, dorsal or ventral). The length parameter provided the most reasonable estimation of the area of the mussel for use in these calculations. The value of length of the mussel is squared to obtain units of square metres (representing an area) which when multiplied by the shear stress term results in a measure proportional to the force. Therefore, the resultant detachment parameter, \( \tau_w l^2 \), represents a measure of detachment strength of zebra mussels.
2.3 Characteristics of Copper

2.3.1 Biofouling Resistance and Copper Toxicity

A second approach to controlling zebra mussel biofouling is to prevent attachment. For several years marine biofouling has been prevented by using copper-containing materials. Cupric oxide has been used in anti-fouling paints and copper metal was used to clad wooden hulls of vessels before the use of copper paints (Blunn and Gareth-Jones, 1988). The anti-fouling mechanism of copper in the marine environment has been attributed to the toxic properties of copper namely, the toxic copper ions that are released into sea water as a corrosion by-product and poison the biofouling organisms (Raju et al., 1988). The minimum copper ion release rate required to prevent biofouling in marine environments was 10 $\mu$m $\cdot$ cm$^{-2}$$\cdot$day$^{-1}$. Alternatively, recent studies have indicated that another toxic copper corrosion by-product, cuprous oxide, was responsible for the anti-fouling characteristics of copper (Raju et al., 1988). Therefore, a clear explanation of the anti-fouling mechanism of copper in seawater has not yet been determined.

Few biofouling studies have been performed in lake water using zebra mussels, however, similar observations of the anti-fouling behaviour of copper-containing materials in seawater have been observed in freshwater environments. Recruitment studies (Dormon et al., 1996; Mackie, 1993) suggest that pure copper and to a lesser extent, copper-nickel alloys (Cu:Ni 90:10, Cu:Ni 80:20, and Cu:Ni 70:30) prevent zebra mussel biofouling. The surfaces of copper-containing materials were protected from biofouling whereas, mussels attached quite readily to surfaces adjacent to the copper. This may be explained by observations
reported for seawater which indicated that copper alloys do not release enough ions into the seawater to prevent adjacent non-copper surfaces from becoming fouled (Boyer and Gall, 1985). However, other references (Wentzell) suggest that it is the copper oxide corrosion by-product which prevents zebra mussel biofouling. A clear explanation of the mechanism of copper which prevents zebra mussel biofouling is lacking and therefore, experiments must be performed to answer this question. It is proposed that one of the corrosion products or the copper ion itself is responsible for its biofouling resistance, although it is not known whether zebra mussels must actually contact the surface.

Although copper is an essential element for life, it can also be toxic (Leckie, 1986). The cupric ion (Cu\(^{2+}\)) has been noted to be the most toxic species of dissolved copper to fish, plants, and other aquatic organisms (Fingerman, 1988; Sweileh, 1987). The toxic properties of copper have been known for many years and led to the use of copper on boat hulls to prevent the attachment of biofouling organisms.

In addition, the toxic effects of copper have been studied in lake water. For example, several investigations have used zebra mussels and other invertebrates as biomonitorers of trace metals in freshwater systems (Kraak, 1991; 1992; Sloof, 1983; Foster, 1978; Anderson, 1977). These studies have shown that copper reduces the filtration rate of zebra mussels, for example; mussels exposed to 90 \(\mu g\cdot L^{-1}\) copper had a filtration rate equivalent to approximately 27% of that of mussels not exposed to copper. Copper also caused the valves of zebra mussels to close at a total copper concentration ranging from 20.8 to 25.6 \(\mu g\cdot L^{-1}\) (Redpath, 1988). Copper also had an effect on the production of byssal threads by zebra
mussels. A reduction in the number of byssal threads placed on a substrate by zebra mussels (Martin, 1975) occurred with an increase in copper concentration in the water. The reduction in mean byssal thread production was followed by a decrease in the percent survival, indicating that copper also has a lethal effect.

Mortality effects of various metals in industrial water systems on zebra mussels have been tested to determine the lethal doses required. A comparison of the properties of five metals; copper, silver, mercury, zinc, and lead, indicated that the copper ions had the strongest effect on the zebra mussels. Exposure to copper concentrations of 4 mg·L⁻¹ for 24 hours resulted in a 100 percent mortality rate, whereas at 1 mg·L⁻¹, all of the mussels died within 48 hours (Dudnikov). The results from these reported studies indicate that copper is toxic and suggests a reason for its effectiveness in preventing zebra mussel biofouling.

Kraak et al. (1993) performed toxicity studies using the parameter EC₅₀ rather than LC₅₀ for comparing the effects of heavy metals in lake water (pH=7.9) on zebra mussels. EC₅₀ is defined as the metal concentration which lead to a 50% decrease in the filtration rate. Kraak et al. concluded from their studies that the sublethal parameter of reduced filtration (EC₅₀) is a far more realistic parameter endpoint for assessing toxicity of heavy metals than mortality. They found that the EC₅₀ filtration rate (48 hours) for zebra mussels exposed to copper was 41 μg·L⁻¹ and that it was the detection of the heavy metals in the water rather than accumulation in the tissue which probably reduced the zebra mussels' filtration rates.

Copper also affects other aquatic organisms and can be ingested in either a bound or free state. For example, toxicity studies using algal samples indicated that copper in the free
or unbound form was available for uptake by algae and resulted in toxic effects. It was suggested in the investigation that nutrients such as phosphorous and nitrogen may directly or indirectly control the effect of a given metal on the algae. Other cations such as Ca$^{2+}$ inhibited copper uptake by algal samples (Stokes, 1983).

2.3.2 Corrosion of Copper

The toxic species of copper are produced through the corrosion of copper. The corrosion of copper exposed to aerated lake water, resulting in the production of by-products, occurs through the following sets of reactions:

**Anodic Reaction:**

\[ \text{Cu} \rightarrow \text{Cu}^+ + e^- \]
\[ \text{Cu}^+ \rightarrow \text{Cu}^{2+} + e^- \]

**Cathodic Reaction:**

\[ \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{OH}^- \]

Therefore, the overall reaction is found by

\[ \text{Cu} \rightarrow \text{Cu}^{2+} + 2e^- \]

and

\[ \frac{1}{2} \text{O}_2(g) + \text{H}_2\text{O}(l) + 2e^- \rightarrow 2\text{OH}^- \]

giving

\[ \text{Cu} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cu(OH)}_2 (s) \]

Various dissolved complexes of copper can form in water, for example; CuO$^0$, HCuO$_2^-$, CuHCO$_3^+$, CuCO$_3^{0}$, and some hydrated species. Thermodynamic data on reactions
between metals and water have been measured, collected and calculated by Pourbaix and are represented in Pourbaix Diagrams (Scully, 1975). Pourbaix Diagrams combine these data with oxide and hydroxide solubility data and equilibrium reaction constants and depict thermodynamically stable phases but do not provide an indication of the rate of corrosion (Scully, 1975). The Pourbaix Diagram shown in Figure 2.2, depicts the stability of soluble copper components within the copper-water system. Figure 2.2 shows that the stable phases present within the copper-water system at a pH of 8 (pH level of lake water) are: Cu, Cu\(^+\), Cu\(_2\)O, Cu(OH)\(_2\) and Cu\(_2\)O\(_3\). In aerated natural waters that have low concentrations of anions and dissolved CO\(_2\), a protective film of cuprous oxide and cupric hydroxide forms on the copper.

Solubilities of various inorganic compounds are given by Seidell (1940). For the copper and nickel species considered in this thesis work the following solubilities are given: 
CuCO\(_3\) - 0.3 mg*L\(^{-1}\), Cu(OH)\(_2\) - 5 mg*L\(^{-1}\), NiCO\(_3\) - 92.5 mg*L\(^{-1}\), and Ni(OH)\(_2\) - 12.7 mg*L\(^{-1}\)
(data is for the given species in water at 18 °C for copper, 20 °C for Ni(OH)\(_2\) and 25 °C for NiCO\(_3\)). These solubilities suggest that nickel requires a higher concentration within water before it precipitates from solution compared to copper.
Figure 2.2: Pourbaix Diagram for the Copper-Water System (reprinted from Pourbaix, 1966).
The corrosion of copper first results in the release of the Cu\(^+\) ion which can combine with oxygen to form cuprous oxide. The corrosion process continues to form Cu\(^+\) which can be oxidized to Cu\(^{2+}\) and combine with the hydroxide ions in the water to produce cupric hydroxide.

Studies have shown that the corrosion products formed on copper do not attach strongly and are often removed by the movement of water. This exposes a fresh surface of copper, preventing organism biofouling (Jones, 1992).

2.3.3 Copper Release Rates

Dormon et al. (1996) showed that copper-containing materials prevented zebra mussel biofouling, however, as the copper content in the alloy decreased the anti-fouling strength of the alloy also decreased. In order to better understand the anti-fouling mechanism of copper-containing alloys in freshwater environments and predict any potential impact associated with its use in preventing biofouling, copper release rates for the various copper-containing alloys were desired. Although numerous corrosion experiments have been previously conducted using copper alloys in various environments, there have not been any studies done which provide the information needed to meet the objectives in this thesis, namely the quantification and comparison of the copper release rate or dissolution rate from copper and copper-nickel alloys into water systems which are similar to those used by Dormon et al. (1996).

In order to meet the objectives set out in this thesis, a large number of journal and related articles have been reviewed which address the behaviour of copper and copper-nickel
alloys in various environments. There have been an extensive number of investigations in which copper corrosion studies were conducted in either acidic, basic or sea water media, because the corrosion rates of copper in these environments are higher than those in fresh water and are easily quantified. However, a limited number of studies have been done which considered the corrosion rates of copper and copper-nickel alloys in tap water and freshwater systems. The results from those studies could not be used for the comparison of the copper release rates from copper-containing alloys in these current studies because they differed in water chemistry and conditions, experimental techniques and analytical methods. These differences are detailed below.

2.3.3.1 Water Chemistry and Conditions

The literature presented in this review includes all investigations related to copper release and corrosion studies. The most relevant articles to this thesis work, which deal with the behaviour of copper in water systems, are highlighted in tabular form (Appendix B). Sea water studies have been included to emphasize the difference in corrosion behaviour of copper in this media compared to that in freshwater systems to indicate that studies in alternate media cannot be extrapolated to freshwater environments. A specific example is the comparison of copper corrosion in sea water with corrosion in fresh water in tropical environments which was studied by Hummer (1968). The loss of copper from copper surfaces exposed to sea water systems is much greater than the losses in freshwater systems.

The conditions studied in the investigations surveyed are different, in many respects, from those used by Dormon et al. (1997). Considering only the investigations concerned
Chapter 2: Literature Review and Theoretical Background

with copper in fresh water (potable, tap or lake/river), it can be noted that the parameters of the media are significantly different compared to both Lake Erie and Lake Ontario water. For example, Seattle tap water has a very low mineral content (Reiber, 1987) and the author suggests that the results presented should not be applied to any other system because this would result in an inaccurate assessment of copper behaviour in these alternate water sources. In many of the distribution systems or tap water systems, the chlorine levels present in the water exceed the quantities in lake water, resulting in different dissolution rates of copper (i.e., compare lake water to sea water) (Wagner, 1991; Alam, 1989; Kasahara, 1988; Schock, 1988; Akkaya, 1987; Hummer, 1968). Some of the experiments were conducted in deionized water which does not contain many of the dissolved species present in the lake water systems and the number and concentration of copper complexes in the two systems is different (Ogino, 1988). Reducing the amount of oxygen in a system or varying the flow rates affects the release rate of copper and represents a different system than that examined in this work (Atlas, 1982; Copson, 1960; Obrecht, 1960). The pH level also has a significant effect on the dissolution rate of copper in any media; lower pH levels generally have higher copper release rates, and therefore, cannot be compared to the system considered in this thesis (Al-Hajjar, 1988; Reiber, 1987; Atlas, 1982). The literature review shows that there has not been any work done under conditions similar to Lake Ontario water and therefore, it was necessary to conduct the copper release rate experiments in order to further understand the anti-fouling mechanism of copper in fresh water.
2.3.3.2 Experimental Techniques

Several techniques have been used in previous studies to quantify the corrosion rates of copper (Appendix B). Some of the analytical techniques used in previous studies included electrochemical techniques, X-ray diffraction, EDAX, XPS, weight loss measurements, pit depth measurements and various concentration measurements. It should be noted that the corrosion activity of a metal entails two processes: Hultquist (1987) states that the corrosion rate of a metal is the sum of the amount of metal leaving its metallic state per unit time (i.e., the amount of metal going into solution (dissolution rate)) and the amount going into compounds on the metal surface per unit time. In this work, the corrosion quantity of importance is the amount of metal going into solution or specifically, the dissolution of copper into lake water. Therefore, it is unnecessary to measure the corrosion rates of the copper and copper-nickel alloys since a direct quantification of the concentrations of copper (the current investigation objective) in the bulk solution is possible. Some of the analytical techniques used in the sea water studies may be applied to certain investigations in freshwater systems; however, the corrosion rates in freshwater systems are very much lower than in other media, and many of these techniques do not have sufficiently low detection limits to accurately quantify the release rates of copper from the metal surface.

Throughout the literature, electrochemical techniques were used to study the corrosion rates of copper in various solutions. These studies did not directly quantify the amount of copper lost to the solution (goal of this thesis) but rather, described a change in corrosion tendency with manipulation of the media parameters (i.e., corrosion inhibitor levels.
Chapter 2: Literature Review and Theoretical Background

and pH. An indirect calculation was done in some cases to relate the electrochemical measurements to a copper loss rate in mils per year (Hilburn, 1983). The loss was found using the electrochemical corrosion measurement which represents the total corrosion rate (loss to solution plus that to oxide) and as mentioned above, quantifies a greater loss than is required to meet the objective of the current investigation.

Brock and Poppelwell (1979) performed laboratory corrosion and release rate studies of copper condenser tube alloys in fresh water. It was found that only 0.1 (10%) of the total weight loss was soluble copper. Conclusions from the study indicated that weight loss measurements were meaningless in determining the copper release rates to the environment since most of the copper lost from the metal was retained in the corrosion product. This conclusion is consistent with the approach taken in this work which utilizes concentration measurements to quantify the release rates of copper.

Pit depth and weight loss measurements are quite common in reported corrosion studies, and are used to quantify the amount of copper lost from the copper surface. The balance used in these measurements must be accurate to a degree depending on the media in which the experiment is conducted; much greater accuracy is required with lower weight loss values as found in freshwater systems. The weight loss technique requires measuring the weight of the sample before and after immersion in the test solution. When the sample is removed it is placed into an acid solution in order to remove the corrosion products. The specimen is then reweighed and the difference in weight between the two measurements represents the loss of copper from the metal surface.
There are some problems associated with the pit depth and weight loss measurement techniques when considered in the context of the current investigation. For instance, the acid may not remove all of the corrosion products formed during exposure to the test media and the weight loss will be lower due to the presence of the remaining metal oxides. Secondly, the acid may remove more than the copper corrosion products; resulting in a greater weight loss. In the investigation performed by Stone et al. (1987), weight loss measurements resulted in errors as large as 19% (from the replicate samples used). Since the current investigation deals with very small corrosion rates, a high degree of accuracy is required, and the weight loss differences may result in significant errors. Furthermore, the quantity determined using the weight loss method includes the loss of copper that has dissolved into solution as well as copper which is present in the form of corrosion products on the metal surface. In this current work the objective, as previously mentioned, is to quantify the amount of copper lost to solution, not the amounts of copper going into the corrosion layer products present on the surface. In sea water solutions, the copper corrosion layer comprises 6.5 to 18.2% of the total copper lost due to corrosion (Beccaria, 1991) (results may be different in freshwater systems). Therefore, if the acid solution method removed all of the corrosion layer, the weight loss technique would overestimate the copper in solution by 6.5 to 18.2% depending on the time frame of the experiment. A further complication is that a variety of metal oxides may be present on the surface of the metal, particularly in the case of copper-nickel alloys. Therefore, in order to accurately determine the amount of copper present in the oxides, experiments must be done to determine the composition of the
corrosion layer (which is dependent on the experimental conditions). In conclusion, the weight loss technique is not a straightforward procedure for quantifying the release rate of copper since quantitative oxide layer analysis would be required. The work required to use a weight loss measurement technique in the current thesis work would probably be greater than that required by the concentration technique, and would be less accurate.

Recent investigations have been performed to study the behaviour of copper in freshwater systems and the preferred analytical technique used to quantify the amount of copper release was a concentration measurement. The methods used to measure concentration included graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma spectrometry (ICP-MS), and neutron activation (NA) (Blume, 1994; Race, 1994; Alam, 1989; Eriksen, 1989; Atlas, 1982). In these experiments, adsorption of copper from the bulk solution onto the walls of the vessels was not quantified and the bulk concentration was used in the final release rate figures. Therefore, the results from these previous studies do not provide an accurate assessment of the behaviour of copper in fresh water and underestimate the release rates in these environments.

Other investigations have used copper concentrations to quantify the loss of copper from copper tubing into the drinking water supply. This was a direct assessment of the release of copper into water which is similar to the information that is required to answer the objectives of this current work. For example, Alum and Sadiq (1989) used an ICP-argon analyzer (inductively coupled plasma) to determine the amount of copper present in drinking water sources (i.e., desalinated sea water with high chlorine levels). The ICP-MS technique
was considered as a method for quantifying the copper concentration in the current studies, but the equipment was not available and graphite furnace atomic absorption spectrometry was suggested as a suitable alternative. The results from Alum and Sadiq (1989) could not be used in the current work because the chlorine levels in the drinking water were much higher than Lake Ontario water and results for copper-nickel alloys were not available.

The study by Beccaria and Crousier (1991) used concentration values (obtained by AAS) of the copper and nickel in solution and in the oxide layer to obtain total weight loss measurements. When using or reviewing concentration results obtained using AAS it must be noted that some of these techniques do not have a high degree of sensitivity below 1 mg L$^{-1}$, where as the GFAAS, which was used in this current work, is sensitive to the order of 0.4 µg L$^{-1}$. Therefore, results from investigations using alternative AAS procedures could not be used in this work. Several previous investigations (for example; Adeloju and Duan, 1994, Beccaria and Crousier, 1991, Lee, 1983) have utilized concentration measurements to quantify the amounts of copper released from copper surfaces which indicates that this method is an acceptable technique and is appropriate for this current work.

Some recent articles have been found which examine copper corrosion. In the study by Reda and Alhajji (1996), the effect of sulfate ion concentration in tap water on copper corrosion was investigated. Values of 55.9 mg·m$^{-2}$·day$^{-1}$ were found after two months of exposure to tap water under stagnant conditions and these values decreased to 34 mg·m$^{-2}$·day$^{-1}$ after eight months. The results from the Reda and Alhajji (1996) study could not be used to infer copper release rates from copper-containing plates into Lake Ontario water for two
reasons. Firstly, these reported results were determined using weight-loss tests which include both the amount of copper lost to the oxide layer as well as the copper dissolved in solution. Since the amount of copper which dissolves into solution is approximately $3\%$ of the total copper lost, the results from this measurement technique cannot be directly compared to the results from the current study. Secondly, the water chemistry and experimental conditions (no aeration mentioned) were not the same as those used in the current studies.

Another article investigated the effect of natural organic matter (NOM) on the corrosion of copper (Rehring and Edwards, 1996). Copper pipes were filled with the test solution and held in a horizontal position with rubber caps covering each end. The copper concentration in a water sample with pH 7.5 and 0 mg NOM$\cdot$L$^{-1}$ was 1 mg$\cdot$L$^{-1}$ after one week and 1.25 mg$\cdot$L$^{-1}$ after eleven weeks. These results could not be used to infer copper release rates from copper plates into Lake Ontario water because the experimental conditions used in those studies i.e., no aeration and the use of rubber stoppers, limits the reaction of the copper which could occur under natural conditions and the adsorption of copper from the solution by the rubber stoppers was not addressed. Moreover, the pH level used in those studies (pH = 7.5) was lower than the pH of Lake Ontario (pH = 8.2) water. Therefore, these results cannot be used to infer a copper release rate value for the system considered in this current work.

A second article by Edwards (Edwards et al., 1996) examined copper by-product release in Boulder tap water which had an average pH of 7.2. Edwards found that exposure time did not influence the release of copper but rather that copper corrosion by-product release was dependent on water quality. At an alkalinity of 100 mg$\cdot$L$^{-1}$ the copper release
rate was 1.5 mg\textsuperscript{L}\textsuperscript{-1} after one week of exposure and 0.45 mg\textsuperscript{L}\textsuperscript{-1} after one month. The conditions of these experiments are consistent with the current study, however in the Edwards' studies, oxygen was limited because the test solutions were held in the piping without aeration which may have affected the formation of the oxide layer on the copper surface and therefore only the effects of the changing solution were noted. Again these studies cannot be directly compared to the current investigations.

The article by Feng et al. (1996) examined the behaviour of copper in tap water which had a pH of 7.6 and chloride content of 65 ppm. The samples were suspended in glass beakers and the vessels were not aerated. The soluble copper concentration in the solution was determined using flame atomic absorption spectrometry (FAAS) and was found to increase linearly with time reaching 1.15 ppm after 500 hours. The copper content in the oxide layer was also examined and the results showed that the copper concentration increased to 8 ppm in approximately 75 hours and then levelled off at a value of 10 ppm by 500 hours. The results from this article cannot be compared to the current study because the water chemistry considered differs from Lake Ontario water. Secondly, Feng et al. assumed that adsorption to the glass vessel was removed by acid treatment but this assumption was not verified. Lastly, the lack of aeration during the experiment may have been a limiting factor in oxide layer formation which would have influenced the results.

Overall, the literature review did not reveal any studies that matched the objectives of the current investigation, namely, to determine the release rate of copper from copper-containing materials into a freshwater environment.
Chapter 3

Zebra Mussel Adhesion Strength Studies

3.1 Introduction

The introduction of zebra mussels (*Dreissena polymorpha* and *D. bugensis*) into North America has impacted ecological and economic systems (Nalepa and Schloesser, 1993; Ludyanskiy et al., 1993; Claudi and Mackie, 1994). These impacts are due to a small set of biological features that are peculiar to zebra mussels and rare in native fauna (Pennak, 1989; Mackie, 1991; Ackerman et al., 1994a). From the perspective of facilities using raw lake water, byssal adhesion is the greatest concern (Claudi and Mackie, 1994). It has been estimated that the economic impact of zebra mussel biofouling in the Great Lakes will reach $5 billion by the next century (Ludyanskiy et al., 1993).

A better understanding of the mechanisms and mechanics of zebra mussel adhesion may provide insight into environmentally benign zebra mussel control and mitigation strategies. One potential zebra mussel control strategy involves the selection of materials and surface preparations that minimize zebra mussel biofouling by reducing larval recruitment and/or reducing their strength of attachment. While there has been considerable interest in the former (Walz, 1973; 1975; Kilgour and Mackie, 1993; Ackerman et al., in review) there are few studies of zebra mussel attachment strength (Ackerman et al., 1992; 1993). These studies have principally described measurement techniques, which have been applied to a limited number of substrates and surface conditions (i.e., smooth) such as aluminum, polymethylmethacrylate, polyvinylchloride, and stainless steel. The nature of the attachment strength of zebra mussels on substrates that are routinely used by residents, municipalities, industries, and marine-related facilities remains to be determined.
While there are a number of attachment strength measurement techniques (review in Ackerman et al., 1993), few can be used with small organisms (e.g., postlarval zebra mussels) or organisms that cannot be easily gripped by conventional testing devices (e.g., algae, sponges, bryozoans, etc.). Moreover, in many situations it is useful to monitor the detachment process under "natural", nonintrusive conditions. In this work, a newly designed wall jet apparatus was used to measure the attachment strength of zebra mussels in a relatively nonintrusive and convenient manner. The results from the wall jet measurements were compared with those obtained using direct mechanical testing.

The goal of this chapter is to compare the strength of attachment of zebra mussels on a variety of commonly used natural, polymeric, and metallic substrates using direct (tensile load) and indirect (wall jet apparatus) mechanical-measurement techniques. These results will provide a basis for the further understanding of the factors that influence attachment strength, and establish guidelines for material selection and water-based cleaning techniques (e.g., water jetting). The results from these tests were used to answer Objectives 1 and 2 of the thesis, namely,

- To develop a methodology to measure the adhesion strength of zebra mussels using a newly-designed wall-jet adhesion strength apparatus; and
- To use the wall-jet and direct mechanical pull-off techniques to measure the detachment strength of zebra mussels as a function of material type and roughness.
3.2 Materials and Methods

3.2.1 Wall Jet Adhesion Strength Measuring System

A wall jet apparatus was designed and constructed to generate fluid forces sufficient to detach zebra mussels from substrates (Figure 2.1). The wall jet is a novel technique for measuring adhesion strength. This method differs from previous zebra mussel attachment strength studies (Ackerman et al., 1992; 1993) because it allows for the direct monitoring of the detachment process under natural, non-intrusive conditions while the studies by Ackerman et al. only measured the detachment strength without the description of the detachment events. An understanding of the events prior to detachment may aid in the development of new cleaning methods for zebra mussel infested materials. In addition, the wall jet provides a novel technique for measuring attachment strength of small organisms or organisms that cannot be easily gripped by conventional testing methods.

The wall jet is produced when a jet of fluid leaves a duct and impinges tangentially on a stationary wall within a quiescent body of fluid (Glauert, 1956; Bakke, 1957; Sigalla, 1958; Schlichting, 1979; Fujisawa and Shirai, 1989). Measurements can be made close to the duct outlet, where the fluid dynamic properties (e.g., velocity distribution, wall shear stress, etc.) of the wall jet are determined by the boundary layer forming on the wall. This provides a reasonably well-defined fluid environment in which to study the adhesion or attachment strength of organisms. Further, the flow characteristics within the wall jet can be conveniently altered by changing the jet flow rate.

In this system, lake water was pumped from a polyvinylchloride (PVC) reservoir, through a 5.08 cm diameter PVC water pipe across a 3.048 cm diameter orifice plate flow meter
and into a 1 m long rectangular duct (2 x 3 cm internal cross section; Figure 3.1). Flow was regulated with a 5.08 cm globe valve downstream of the orifice plate flow meter and was determined by differential pressure measurements across the previously calibrated orifice plate flow meter. The duct emptied into a water-filled holding chamber at a 3° angle to the horizontal, creating a wall jet that impinged on a plate (8 cm by 16 cm) placed at the outlet of the duct. To facilitate access to mussels in different locations on the test plate, the duct was positioned in one of two configurations: (1) in the down position, the upper surface on the bottom wall of the duct was flush with the test plate, and (2) in the up position, the duct rested on the surface of the test plate with the upper surface of the bottom wall 1 mm above the test plate (Figure 3.1B). Water returned to the reservoir by draining out of the holding tank, over a gate. The holding tank was fitted with glass viewing ports to permit video microscopy. The positioning of mussels and test plates is described below.

In order to characterize the fluid dynamics of the wall jet on the test plate at each flow rate, the wall shear stress ($\tau_w$) was determined in both the duct-up and duct-down configurations using a modified Preston tube (Winter, 1977; Nitsche et al., 1985). The feasibility of using a Preston-static tube for the measurement of wall shear stress is described in detail by Ackerman et al. (1994 b). Seventy-five measurements of $\tau_w$ were made on a grid of (x,y) locations on the surface of a single, smooth test plate, where x is the downstream position from the duct outlet and y is the transverse position measured from the duct centreline. Measurements in the interval $0 \leq x \leq 13$ cm (14 cm in the duct-down configuration), $0 \leq y \leq 3$ cm were used to generate contour plots of $\tau_w$ (see Figure 3.1) for each flow rate used in this study. As well, the
shear stress on the centreline of the lower wall of the duct 1.4 cm upstream of the duct outlet (i.e., within the duct) was determined using the Preston tube.

In this work, the shear stress contours measured on a smooth test plate were taken to be representative of the shear stresses which would exist on all test plates, independent of plate roughness. The smooth plate shear stress contours were therefore used to determine the nominal shear stress acting on zebra mussels during the detachment experiments (see below).

### 3.2.2 Experimental Procedure

Test plates (8 cm by 16 cm, see Table 3.1a for plate material description) of various construction materials were deployed at a minimum depth of 1.5 m in the forebay of Ontario Hydro’s Nanticoke Thermal Generating Station, Nanticoke, Ontario, (NTGS; Lake Erie) in May 1991. A number of test plates were collected in the winter, spring, and summer of 1992. Fortunately, mussels of this size (mean values between 7.3 mm and 12.2 mm) could be gripped in a tensile loading device to permit independent validation of the wall jet measurements. At the time of collection, lake water and test plates or rock samples (limestone 85 % and dolomite 15 %: Niagara Escarpment; Hewitt and Vos, 1972) from a minimum forebay depth of 1 m were transported from NTGS to the laboratory where they were maintained at 8 - 12 °C for up to 1 month. During that time the substrates (rocks and test plates) were kept in aerated lake water aquaria under a 12 hour light: 12 hour dark cycle with constant filtration. Mussels attached to substrates were fed a mixture of live *Chlorella emersonii* and *Selenastrum capricornutum* (UTCC-86 and UTCC-37, respectively; University of Toronto Culture Collection, Department of Botany). Water changes were conducted at least once a week and the dissolved oxygen, temperature and pH of each aquarium were monitored (for lake water analysis see Table 4.2).
Table 3.1a: Materials, Surface Preparation, and Surface Roughness of Test Plates used in this Work

<table>
<thead>
<tr>
<th>Code</th>
<th>Material and composition</th>
<th>Preparation</th>
<th>Mean (μm)</th>
<th>St. Error (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Natural Substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>WOOD</td>
<td>Varnished marine plywood</td>
<td>Smooth</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>CONC</td>
<td>Marine concrete</td>
<td>Smooth</td>
<td>1.07</td>
<td>0.09</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>Rough</td>
<td>2.9</td>
<td>0.2</td>
</tr>
<tr>
<td>ROCK</td>
<td>Dolomite/limestone cobble</td>
<td>Rough</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Polymeric Substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CT-E</td>
<td>Coal-tar epoxy coated STEEL</td>
<td>Smooth</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethylmethacrylate (plexiglass; acrylic)</td>
<td>Smooth</td>
<td>0.012</td>
<td>0.002</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene (Teflon)</td>
<td>Smooth</td>
<td>0.66</td>
<td>0.02</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>Medium</td>
<td>&gt;5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>Rough</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinylchloride</td>
<td>Smooth</td>
<td>0.044</td>
<td>0.005</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>Medium</td>
<td>&gt;5</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>Rough</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Metallic Substrates</td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL</td>
<td>Aluminum (alloy 6066-T6)</td>
<td>Smooth</td>
<td>0.28</td>
<td>0.02</td>
</tr>
<tr>
<td>70:30</td>
<td>Copper:Nickel (alloy 715)</td>
<td>Smooth</td>
<td>0.311</td>
<td>0.006</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>Medium</td>
<td>0.64</td>
<td>0.05</td>
</tr>
<tr>
<td>STEEL</td>
<td>Mild steel</td>
<td>Smooth</td>
<td>2.7</td>
<td>0.2</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>Medium</td>
<td>2.6</td>
<td>0.6</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>Rough</td>
<td>&gt;4.5</td>
<td></td>
</tr>
<tr>
<td>SS</td>
<td>Stainless Steel (alloy 304)</td>
<td>Smooth</td>
<td>0.099</td>
<td>0.006</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>Medium</td>
<td>0.33</td>
<td>0.02</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>Rough</td>
<td>0.84</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Except where stated, the zebra mussels examined in this study, and the majority of mussels (i.e., > 90 %) that recruited at the field site, were *D. bugensis* (the quagga mussel), which has a tapered ventral surface (May and Marsden, 1992; Domm et al., 1993; Rosenberg and Ludyanskiy, 1994). The "typical" zebra mussel (*D. polymorpha*) has a flat, slightly concave ventral surface.

Prior to an experiment, substrates were removed from the maintenance facility and allowed to acclimatize to room temperature (15 - 17 °C) overnight, or for a minimum of 3 hours in aerated lake water. As a result of the strong recruitment of larvae in 1991, the majority of mussels, which formed a multiple layer on the substrates, were carefully removed from the substrates to provide relatively isolated mussels for wall jet testing. This was desirable to avoid mussel-mussel fluid-mechanical interactions. Mussel removal (i.e., detachment from the substrate) was accomplished by holding the mussel in forceps or in the spring-loaded grips of a precision scale (100, 300, and 500 g capacity; Switzerland) and pulling normal to the face of the substrate. In the case of mussel removal using the force scale, the attachment strength was inferred from the tensile load [detachment force (DF, Newtons)] and was recorded so as to allow a comparison of direct mussel pull-off data with the wall jet measurements and to compare zebra mussel adhesion with published results from other species. The load was applied at a constant rate (e.g., ≈ 0.5 N·s⁻¹ for 100 g scale). Approximately 10-15 isolated target mussels remained on the test plate after the mussel removal protocol. In addition, any algae or sediment was also removed from the plate surface to ensure that the flow reached the designated target mussel unimpeded. The copper-nickel 70:30 plates were not tested in the wall jet apparatus in order to avoid copper contamination of the system resulting from corrosion of
the alloy. Instead, the mussels attached to the copper-nickel 70:30 surfaces were tested using only the spring scale.

Most wall jet tests were carried out with the duct in the "down" configuration (interior surface of duct lower wall flush with plate surface). Care was taken to ensure that the portion of the substrate to which a mussel was attached was level so as to maintain the 3° angle between substrate and duct. The substrate was shifted until the mussel under investigation was within y = 1.0 cm of the centreline of the duct, and its x and y positions were noted. The initial orientation of each mussel, with respect to the opening of the duct, was also recorded.

Water flow through the wall jet was increased incrementally until mussel detachment was observed and recorded using video microscopy. More specifically, beginning at time zero, the flow control valve was opened slowly (e.g., ≈ 1.38 x 10⁻⁴ m³s⁻²) to a flow rate of 1.38 x 10⁻³ m³s⁻¹ corresponding to a 3 cmHg (1 cmHg = 1.33 kPa) differential pressure across the orifice plate flow meter. This flow rate was maintained for 30 s, after which the flow was again increased by a differential orifice plate pressure of 3 cmHg. This procedure was repeated until the mussel detached, or until the maximum flow rate of 4.5 x 10⁻³ m³s⁻¹ was reached. The adhesion strength of zebra mussels was inferred from the fluid detachment parameter (DP, pascals x square metre) calculated from the product of the nominal wall shear stress (τₜ) at the point of detachment and the square of the mussel length (l, metres; i.e., DP = τₜl², see Section 2.2). As described in Section 2.2, τₜl² is proportional to the detachment force differing by only a constant.
Chapter 3: Zebra Mussel Adhesion Strength Studies

3.3 Results

3.3.1 Wall Jet Fluid Flow Characteristics

Based on calibration tests for the orifice plate flow meter, the average velocity in the duct ranged from 2.3 m/s at an orifice plate differential pressure of 3 cmHg to 7.5 m/s at 33 cmHg. This corresponds to duct-corrected Reynolds numbers, $Re_{duct}$, from $6 \times 10^4$ to $2 \times 10^5$ where

$$Re_{duct} = \Phi \frac{d_h V}{\nu}$$

and $\Phi = 1.074$ is the form coefficient of the duct (Jones, 1976), $d_h$ is the duct hydraulic diameter (metres), $V$ is the average fluid velocity in the duct (metres per second), and $\nu$ is the kinematic viscosity (square metres per second). Based on these values of $Re_{duct}$ the flow was fully developed and turbulent at the outlet of the duct. The measured centreline wall shear stress ($\tau_w$) within the duct ($x = -1.4$ cm, $y = 0$ cm) ranged between 13.3 and 117 Pa for this range of flows.

The $\tau_w$ contour maps were generated using the results from the measurements taken using the Preston-static tube in the wall jet under various flow rates. The pressure differentials measured using the Preston-static tube were used in equation (2.8). This value was then substituted into equation (2.9) and using equation (2.7) the values for $\tau_w$ were determined. These $\tau_w$ values were plotted in the form of contour maps which can be used to determine the wall shear stress for each position on the test substrates used in the wall jet tests.

The $\tau_w$ contour maps at different flow rates shared a number of common features (Figures 3.1A and B). The highest $\tau_w$ values were found directly before the wall jet along the projection of the duct centreline. A steep cross-stream gradient in $\tau_w$ was observed at $y \approx 1.5$
cm close to the duct (x = 0 cm) and at greater y distances as the distance from the duct increased. This is what would be expected as the 3 cm wide jet gradually grows in width as x increases. Differences in $\tau_w$ maps between the two duct positions were noted, including (1) generally higher $\tau_w$ values in the duct-down configuration, and (2) a steep downstream gradient in $\tau_w$ between x = 0 cm and x $\approx$ 1.5 cm in the duct-up configuration.

Figure 3.1: Wall Shear Stress ($\tau_w$, Pa) contours on the surface of a smooth plate at a flow rate of $4.5 \times 10^{-3} \text{ m}^3\cdot\text{s}^{-1}$ for (A) Duct-up and (B) Duct down configurations (x and y are expressed in cm).
3.3.2 Adhesion Strength of Zebra Mussels

The detachment of mussels from substrates using the wall jet depended on the original orientation of a mussel relative to the duct. As soon as flow was initiated, mussels lifted slightly off the substrate, indicating that they were being held in place by tension in their byssal threads. Generally, when flow impinged anywhere except directly on the left or right valves, mussels twisted about their byssus until they were perpendicular to the flow (i.e., so that the flow was directed towards the valves). As the flow was increased, they began to oscillate (~7 Hz) about their byssal connections in the plane of the surface and finally detached from the surface. While not measured in this study, observations during testing indicated that detachment occurred through a combination of three mechanisms: (1) failure of the byssal pad, (2) failure of the byssal thread, and (3) failure of the byssal stem at the insertion of the retractor muscle. The detachment event was rapid and generally occurred within 30 s of an increase in the jet flow rate. Once detached, a mussel moved downstream and upwards from its original position. Some mussels formed new byssal attachments to the walls of the reservoir tank. There were on average 5 ± 1% of mussels, however, that did not detach at the maximum wall jet flow of 4.5 x 10^{-3} m^3s^{-1}, for a given substrate (see Table 3.1b).

Mussels detached under a range of fluid DP values. These DP results were generally normally distributed (13 of 19 cases of material and roughness comparisons; Kolmogorov-Smirnov test) and there was generally a significant regression of DP on mussel length (P < 0.05 in 15 of 19 cases, see Appendix A). Overall, the mean DP required to remove zebra mussels ranged from 2.0 ± 0.2 x 10^{-3} Pa*m^2 (mean ± standard error) on smooth PTFE to 12 ± 1 x 10^{-3} Pa*m^2 on medium STEEL (see Table 3.1a for notation, Figure 3.2). With the exception of
Table 3.1b: Fluid Detachment Parameter (DP) of Zebra Mussels (Dreissena bugensis) on Natural, Polymeric, and Metallic Materials of Differing Surface Roughness

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface roughness</th>
<th>Number of Mussels</th>
<th>DP $\times 10^{-3}$</th>
<th>Mussel Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Remaining</td>
<td>Detached</td>
<td>Mean (Pa$\cdot$m$^2$)</td>
</tr>
<tr>
<td>CONC</td>
<td>Smooth</td>
<td>1</td>
<td>26</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>Rough</td>
<td>1</td>
<td>30</td>
<td>6.3</td>
</tr>
<tr>
<td>WOOD</td>
<td>Smooth</td>
<td>1</td>
<td>33</td>
<td>6.6</td>
</tr>
<tr>
<td>ROCK</td>
<td>Rough</td>
<td>11</td>
<td>55</td>
<td>8.9</td>
</tr>
<tr>
<td>Natural Substrates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CT-E</td>
<td>Smooth</td>
<td>0</td>
<td>23</td>
<td>7.5</td>
</tr>
<tr>
<td>PMMA</td>
<td>Smooth</td>
<td>1</td>
<td>53</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0</td>
<td>12</td>
<td>5.7</td>
</tr>
<tr>
<td></td>
<td>Rough</td>
<td>1</td>
<td>23</td>
<td>6.2</td>
</tr>
<tr>
<td>PVC</td>
<td>Smooth</td>
<td>0</td>
<td>58</td>
<td>5.6</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>4</td>
<td>29</td>
<td>7.8</td>
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<td>Rough</td>
<td>0</td>
<td>23</td>
<td>5.8</td>
</tr>
<tr>
<td>Polymeric Substrates</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AL</td>
<td>Smooth</td>
<td>1</td>
<td>28</td>
<td>4.2</td>
</tr>
<tr>
<td>STEEL</td>
<td>Smooth</td>
<td>2</td>
<td>27</td>
<td>10.5</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>2</td>
<td>18</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Rough</td>
<td>2</td>
<td>16</td>
<td>10.8</td>
</tr>
<tr>
<td>SS</td>
<td>Smooth</td>
<td>2</td>
<td>73</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0</td>
<td>26</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>Rough</td>
<td>2</td>
<td>29</td>
<td>7.3</td>
</tr>
<tr>
<td>Metallic Substrates</td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
CONC and STEEL, mean DP values differed within roughnesses of a given substrate. The greatest attachment strength, as inferred from DP, was observed on natural substrates, where the mean DP ranged from 6.3 ± 0.5 x 10^{-3} Pa·m^2 on rough CONC to 7.4 ± 0.5 x 10^{-3} Pa·m^2 on smooth CONC, and metallic substrates, with values ranging from 4.2 ± 0.5 x 10^{-3} Pa·m^2 on AL to 12 ± 1 x 10^{-3} Pa·m^2 on medium STEEL. Mussel attachment was generally lower on polymeric substrates, with values ranging from 2.0 ± 0.2 x 10^{-3} Pa·m^2 on smooth PTFE to 7.8 ± 0.7 x 10^{-3} Pa·m^2 on medium PVC. In terms of ranking of substrate type, the values on AL were more similar to polymeric substrates, while those observed on PVC were more typical of metallic substrates.

The attachment strength results, as inferred from the tensile DF required to detach mussels, were consistent with those obtained from wall jet testing. These results were normally distributed approximately half the time (10/21 cases) and there was a statistical relationship between mussel size and DF (i.e., P < 0.05 in 17/21 cases, see Appendix A). The mean DF ranged from 0.18 ± 0.04 N on smooth PTFE to 1.6 ± 0.2 N on smooth STEEL, which ranked second in DP (see Table 3.1c and Figure 3.3). Among surface roughness, the mean DF were similar for CONC, STEEL, and PVC, but different among roughnesses of PTFE and SS. The highest mean DF were again found among metallic substrates, where values ranged from 0.46 ± 0.05 N on AL to 1.6 ± 0.2 N on smooth STEEL. Interestingly, the DF values measured on 70:30 were more similar to the other metallic substrates than those on AL, which was consistently low by both methods. The natural substrates were next with values ranging between 0.60 ± 0.05 N on rough CONC to 1.55 ± 0.07 N on ROCK (DF=1.4 ± 0.4 N for
With the exception of ROCK, these values were similar to polymeric materials, where mean DF ranged from \(0.18 \pm 0.04\) N (smooth PTFE) to \(0.94 \pm 0.08\) N (CT-E).

Table 3.1c: Detachment Force (DF) of Zebra Mussels (Dreissena bugensis and D. polymorpha) on Natural, Polymeric, and Metallic Materials of Differing Surface Roughness

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface roughness</th>
<th>Number of Mussels</th>
<th>Detachment Force (DF)</th>
<th>Mussel Length</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Remaining</td>
<td>Detached</td>
<td>Mean (N)</td>
</tr>
<tr>
<td><strong>Natural Substrates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CONC</td>
<td>Smooth</td>
<td>0</td>
<td>65</td>
<td>0.67</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>62</td>
<td>0.60</td>
</tr>
<tr>
<td>WOOD</td>
<td>Smooth</td>
<td>0</td>
<td>122</td>
<td>0.72</td>
</tr>
<tr>
<td>ROYK</td>
<td>Rough</td>
<td>0</td>
<td>324</td>
<td>1.55</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>26</td>
<td>1.4</td>
</tr>
<tr>
<td><strong>Polymeric Substrates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CT-E</td>
<td>Smooth</td>
<td>0</td>
<td>77</td>
<td>0.94</td>
</tr>
<tr>
<td>PMMA</td>
<td>Smooth</td>
<td>0</td>
<td>38</td>
<td>0.35</td>
</tr>
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<td>15</td>
<td>0.18</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>0</td>
<td>60</td>
<td>0.75</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>45</td>
<td>0.80</td>
</tr>
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<td>Smooth</td>
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<td>0.87</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>0</td>
<td>60</td>
<td>0.9</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>48</td>
<td>0.8</td>
</tr>
<tr>
<td><strong>Metallic Substrates</strong></td>
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<td></td>
</tr>
<tr>
<td>AL 70:30</td>
<td>Smooth</td>
<td>0</td>
<td>36</td>
<td>0.46</td>
</tr>
<tr>
<td>-</td>
<td>Smooth</td>
<td>0</td>
<td>34</td>
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<td>-</td>
<td>Medium</td>
<td>0</td>
<td>30</td>
<td>1.1</td>
</tr>
<tr>
<td>STEEL</td>
<td>Smooth</td>
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<td>32</td>
<td>1.6</td>
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<tr>
<td>-</td>
<td>Medium</td>
<td>0</td>
<td>55</td>
<td>1.5</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>28</td>
<td>1.3</td>
</tr>
<tr>
<td>SS</td>
<td>Smooth</td>
<td>0</td>
<td>76</td>
<td>0.67</td>
</tr>
<tr>
<td>-</td>
<td>Medium</td>
<td>0</td>
<td>55</td>
<td>0.77</td>
</tr>
<tr>
<td>-</td>
<td>Rough</td>
<td>0</td>
<td>61</td>
<td>1.1</td>
</tr>
</tbody>
</table>
Chapter 3: Zebra Mussel Adhesion Strength Studies

Figure 3.2: Mean Fluid Detachment Parameter (DP) required to remove zebra mussels (Bar = mean ± standard error; numerical value = sample size).

Figure 3.3: Mean Detachment Force (DF) required to remove zebra mussels (Bar = mean ± standard error; numerical value = sample size).
3.3.3 Statistical Analysis

In the analysis of these results it was assumed that mussel detachment is a threshold event and not due to fatigue caused by previous testing at lower flow rates. This assumption is based on a test in which a mussel that was exposed to low flow rates (< 3.06 x 10^{-3} m^3s^{-1}) remained attached for over 2.5 hours. Detachment finally occurred when the flow was increased to 3.06 x 10^{-3} m^3s^{-1}. This observation was taken as support for the assumption that detachment is indeed a threshold effect. Bearing this in mind, the data were analyzed statistically using a hierarchical (or nested) analysis of variance (ANOVA), which allowed the variance to be partitioned first among materials and second among roughnesses within a material. Satterthwaite's approximation was used in all cases due to unequal sample sizes (Sokal and Rohlf, 1981). Planned comparisons [Fisher's least significant differences (LSD)] were run to determine the relationship among pairs of materials.

There were significant differences in attachment strengths among materials as measured by the DP (F = 3.73, P < 0.05; Table 3.2). Attachment strength varied significantly among pairs of materials from natural or metallic substrates and polymeric substrates (Table 3.3). Certain materials did not, however, follow the trend within their category. For example, AL was more similar to polymeric substrates, PVC was similar to natural and metallic substrates, and SS was at the low range for natural and metallic substrates. Significant differences were detected among roughnesses within materials in the second level of the ANOVA (F = 6.23, P < 0.001; Table 3.2). Surface roughness differences were found in the following pairs of comparisons, using separate single classification ANOVAs: smooth PTFE and medium PTFE, and smooth PTFE and rough PTFE at P < 0.001; smooth PVC and medium PVC, and medium PVC and...
rough PVC at P < 0.05; smooth SS and medium SS, and smooth SS and rough SS at P < 0.001.

Table 3.2: Hierarchical Analysis of Variance (using Satterthwaite’s Approximation) of mean detachment parameter (DP) required to detach zebra mussels from Natural, Polymeric and Metallic materials of difference surface roughness

<table>
<thead>
<tr>
<th>Level (1)</th>
<th>Sum of squares (2)</th>
<th>Degrees of freedom (3)</th>
<th>Mean squares (4)</th>
<th>F statistic (5)</th>
<th>Probability (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>0.0030</td>
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<td>0.00033</td>
<td>3.7294</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Roughness</td>
<td>0.0006</td>
<td>8.2</td>
<td>0.00009</td>
<td>6.2295</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>Error</td>
<td>0.0083</td>
<td>586</td>
<td>0.00001</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total</td>
<td>0.0119</td>
<td>604</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.3: Analysis of Variance for Detachment Parameter

Analysis of Variance (ANOVA) of zebra mussel adhesion strength on a variety of materials, as inferred from the detachment parameter, $\tau_1$, measured in the wall jet. (. = P > 0.05, * = P < 0.05, ** = P < 0.01, *** = P < 0.001)

Matrix of Pairwise Comparisons (Fisher’s Least Significant Difference)
The results of the DF analyses correlated with those for DP, although one additional material was included (Cu:Ni 70:30; Table 3.4 and Figure 3.4). Significant differences were detected among materials in terms of DF ($F = 11.27, P < 0.01$; Table 3.4). The number of significantly different pairwise comparisons was similar (37/55 for DF; 32/45 for DP), although their distribution among substrate types was somewhat different (Figure 3.4). Most of the significant differences occurred between the highest DF materials (natural and metallic substrates: ROCK, STEEL, and 70:30), the lowest DF materials (polymeric and metallic substrates: PTFE, PMMA, and AL). As in the case of DP, there were significant differences among roughnesses within materials (second level of the ANOVA; $F = 2.34, P < 0.05$; Table 3.4), with significantly greater attachment observed on rougher PTFE ($P < 0.001$ for smooth PTFE and medium PTFE, and smooth PTFE and rough PTFE) and SS ($P < 0.001$ for smooth SS and rough SS, $P < 0.05$ for medium SS and rough SS; not presented). However, in the case of STEEL, it was noted that the detachment force required to remove mussels decreased with surface roughness but these adhesion strength differences were found to be not significant.

3.4 Discussion

3.4.1 Wall Jet Characterization

The measured fluid dynamic characteristics of flow within the duct agreed well with the results of other empirical studies of flow in rectangular ducts of differing aspect ratio (Dean, 1978; Knight and Patel, 1983; Leutheusser, 1984). In the current case, the expected centreline wall shear stress on the lower surface of the duct (aspect ratio of 1.5) is given by

$$\tau_0 = \frac{f_{\text{corr}} \rho u^2}{d},$$

where $f_{\text{corr}}$ is the friction factor corrected for duct flow (see Equation 3.1) and $\rho$ is the fluid density.
\[ \tau_{cl} = 1.09 \frac{f_*}{8} \rho V^2 \]  

(3.2)

Table 3.4: Hierarchical Analysis of Variance (using Satterthwaite’s Approximation) of mean tensile force (DF) required to detach zebra mussels from Natural, Polymeric and Metallic materials of difference surface roughness

<table>
<thead>
<tr>
<th>Level</th>
<th>Sum of squares (2)</th>
<th>Degrees of freedom (3)</th>
<th>Mean squares (4)</th>
<th>F statistic (5)</th>
<th>Probability (6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
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<td>10</td>
<td>16.70</td>
<td>11.27</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Roughness</td>
<td>11.6</td>
<td>6.3</td>
<td>1.48</td>
<td>2.34</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Error</td>
<td>924.6</td>
<td>1461</td>
<td>0.63</td>
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<td>1481</td>
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Table 3.5: Analysis of Variance for Detachment Force

ANOVA of zebra mussel adhesion strength on various materials, as inferred from the detachment forces measured using the spring scale tensile load technique. ( = P > 0.05, * = P < 0.05, ** = P < 0.01, *** = P < 0.001)

<table>
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<tr>
<th></th>
<th>AL</th>
<th>CONC</th>
<th>CT-E</th>
<th>PMMA</th>
<th>PVC</th>
<th>ROCK</th>
<th>SS</th>
<th>STEEL</th>
<th>PTFE</th>
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(kilograms per cubic metre) (Knight and Patel, 1983). The $\tau_w$ measured within the duct was on average within 1.1% of the values predicted by Equation 3.1 in the down configuration and within 3.3% in the up configuration.

The $\tau_w$ patterns observed on the test plate were more complicated than those observed within the duct (Figure 3.1). Data are not available for independent verification of the $\tau_w$ mappings, but the general features of these maps can be compared with $\tau_w$ inside the duct. For example, one would expect the $\tau_w$ a short distance downstream of the duct to be similar to that within the duct. This occurred several centimetres downstream in the up configuration, where the local maxima in $\tau_w$ were on average within 0.1% of that in the duct. However, in the down configuration, the maxima $\tau_w$ were on average 16% larger than in the duct. This difference may be in part due to streamline curvature following impingement, due to the $3^\circ$ inclination of the duct.

These results indicate that the wall jet provides a reasonably well-defined flow environment in which to measure the bulk properties of adhesion or attachment strength of benthic organisms such as zebra mussels. It is important to note that the current design is limited to small organisms (i.e., $< 2$ cm in height) that can be detached by a nominal wall shear stress ($\tau_w$) less than 130 Pa. The latter limitation could be overcome by an increase in pumping and tank capacity, while the former would require a larger duct.

The $\tau_w$ values presented in this study are nominal values, for several reasons. Firstly, $\tau_w$ contour maps were made without mussels present; the presence of a mussel would influence the flow pattern and thus change the $\tau_w$ distribution. Secondly, $\tau_w$ contour maps were determined on a smooth plate using a Preston tube which had been calibrated for flow over a hydraulically
smooth surface. The fact that some of the substrates were rough means that the actual $\tau_w$ values would deviate somewhat from the nominal $\tau_w$ values. However, because the Preston tube diameter (1 mm) is larger than the viscous sublayer thickness ($\leq 0.2$ mm for flow rates of interest), this effect is not expected to be substantial, so long as $\tau_w$ is interpreted as the shear stress which would have existed on a smooth surface at that particular flow rate. Ultimately, the validity of using the nominal $\tau_w$ to characterize the mussel attachment strength is confirmed by the excellent correlation between DF and DP presented in Figure 3.4. If the $\tau_w$ values were grossly in error due to the effects described above, the strong correlation observed would not be expected.

### 3.4.2 Attachment Strength of Zebra Mussels

In many respects, the inferences of zebra mussel attachment strength for both methods correlated well. This was evident from a plot of DP versus DF, which was linear with a clear separation of materials of weak and strong attachment (Figure 3.4). For example, the results of both techniques revealed that zebra mussels adhered least strongly to PTFE, PMMA, and AL, and most strongly on ROCK and STEEL. There were many materials of intermediate mussel attachment that were similar in attachment strength as inferred by both techniques (Figure 3.4). In practice, however, detachment via fluid forces is more realistic ecologically, and from the perspective of removal technologies (e.g., water jetting) within water-distribution networks.

Several patterns in the attachment strength of mussels on substrate type were evident and were statistically significant. The strongest attachment was found on natural substrates, followed by metallic, and then polymeric ones (i.e., natural $\geq$ metallic $>$ polymeric; Table 3.6). These generalizations did not always hold, as in the case of PVC, where results were more
Figure 3.4: Correlation between the results from the two adhesion strength test methods.

Table 3.6: Comparison of Fluid Detachment Parameter and Tensile Force required to detach zebra mussels from natural, polymeric and metallic material categories.
similar to those of "stronger" substrates (natural and metallic). This can be contrasted with results on AL, where attachment strengths were lower than the other metallic substrates. Possible explanations for these deviations may be related to the chemistry of the substrate surface where leaching and/or corrosion may have influenced attachment. For PVC, the possible leaching of phenolic-like compounds in the plasticizer and stabilizers (National Sanitation Foundation, 1992) may have enhanced the bonding and thus attachment strength relative to the other polymers. Conversely, the leaching of aluminum ions from the surface may have limited mussel attachment (Pillai and Ravindran, 1988). Similar trends in attachment strength were observed on PVC and AL when they were examined with a rotating disk test device (Ackerman et al., 1992). The relatively high mussel attachment on 70:30 appears to contradict these arguments given the toxic nature of copper ions (Fisher et al., 1984). In this situation, however, the formation of an oxide layer may have eliminated or reduced the leaching rate of copper ions (Efird, 1976; Pillai and Ravindran, 1988; Raju et al., 1988). The antifouling behaviour of copper and copper-nickel alloys is discussed further in the subsequent chapters.

These differences in mussel attachment strength are relevant for zebra mussel control strategies, especially those that provide design guidelines for material selection and surface preparation. Admittedly, while a wide selection of commonly used materials was examined, this represented only a fraction of possible substrates. Nonetheless, the current observations that attachment strength could be grouped into ranges according to material types (natural, metallic, and polymeric) suggests that, as a first approximation, the attachment strength of other materials could also be estimated to fall within one of these ranges.
It should be noted that these results are based largely on measurements of mussels that had been resident in the lake for approximately one calendar year. The dependence of mussel size (see Appendix A) on attachment strength suggests that the results for older and larger mussels may be different than the limited range in mussel sizes reported here. This was also noted in a recent study by Dormon et al. (1997) whose comparison of adhesion strength results to the current results indicated that their values were two and three times larger. There were two possible explanations given for the difference. Firstly, the mussels in the Dormon et al. study had recruited to the plates over a two year period rather than one year and secondly, the mussels were 30-75% larger and probably had more threads. There is also a possibility that attachment strength may vary according to the zebra mussel species. While these results were obtained principally from *Dreissena bugensis*, a DF comparison with *Dreissena polymorpha* on ROCK indicated that the two species were functionally similar in attachment strength. Lastly, the detachment force required to remove individual mussels from dense, many-layered aggregations would be greater than those for the isolated mussels examined here.

Obviously, the most desirable situation for control would be one in which zebra mussels did not recruit or adhere to materials. Unfortunately, there are presently few materials that satisfy these requirements without being potentially damaging to the environment or too costly (Fisher et al., 1984; Claudi and Mackie, 1994). An alternative is to use materials or surface preparations on which zebra mussel attachment is reduced, to facilitate removal and cleaning. The use of smooth polymers, other than PVC, would facilitate these goals at some expense. On the other hand, "untreated" natural and metallic substrates would not. Simple treatments of these substrates, such as eliminating the heavy corrosion (scale) of mild steel through the use of
coal tar epoxy coating, significantly reduced mussel attachment strength (Tables 3.2 and 3.4, Figures 3.2 and 3.3).

3.4.3 Adhesion Strength Theory

It is difficult to account for the observed differences in attachment strength among substrates on a purely theoretical basis (e.g., Waite, 1983; Mihm and Loeb, 1992; Ackerman et al., 1993). There are certainly a number of properties of substrates that may affect the bonding and, therefore, the attachment strength of byssally attached bivalves. These include a combination of: (1) the surface free energy ($\gamma$) affecting the spreading of the byssal adhesive on the substrate; (2) the chemical composition of the substrate and its relation to adhesion adsorption, diffusion, and specific chemical interactions; and (3) the microtopography of the substrate as it affects the mechanical interlocking of the adhesive (Waite, 1983; Kinloch, 1987; Ackerman et al., 1993). However, while the nominal surface free energy of clean substrates and thus the size of the byssal adhesive pad has been implicated in the adhesion of Mytilus (Crisp et al., 1985), it does not appear to apply here as an overriding factor, since there is no consistent relationship between attachment strength and $\gamma$ of the clean substrate. While the attachment strength does not appear to be influenced greatly by the surface free energy of the clean substrates, the actual $\gamma$ of the "biofilmed" surface remains to be determined. This may be immaterial, however, since it has been reported that the byssal pad displaces the biofilms to contact the substrate directly (Baier et al., 1992).

On a macroscopic scale, the roughness of the substrate can be used as an inference of the possible degree of mechanical interlocking. Visually, rocks had greater porosity and macroscopic roughness than the material test plates, except STEEL test plates, which became
heavily corroded. The higher adhesion strength values may be the result of the plaque filling the roughness features of the surface creating a stronger bond via mechanical interlocking and increased interfacial area and, therefore, the adhesion strength depends on the substrate characteristics.

This hypothesis was confirmed through a recent study conducted by our group which explored the zebra mussel modes of detachment from various materials including CONC, SS, STEEL, PVC, and PTFE (Dorman et al., 1997). The results from the study showed that the modes of detachment, for example, thread breakage or plaque failure, varied with material. Specifically, materials which displayed lower zebra mussel adhesion strength, e.g., PTFE, had more plaque (adhesive connecting byssal threads to the substrate) failures where as there were more threads broken (more plaques remained) on materials which required higher forces for detachment, e.g., STEEL which had a rougher surface resulting from corrosion. This result indicates that the strength of byssal plaque attachment is dependent on the substrate which affects the adhesion strength of zebra mussels. However, it was also suggested that as the strength of adhesion between the substrate and plaque increases, the dominant mode of failure for detachment is thread rupture. At this point, the detachment strength is dependent upon the strength of the byssal threads, which is independent of the substrate (Dorman et al., 1997)

3.5 Conclusions

In this Chapter it was shown that the wall jet apparatus provided a useful technique for the measurement of zebra mussel adhesion strength and the observation of the events preceding the detachment of the mussel which cannot be determined when using other non-intrusive methods. In addition the wall jet has several advantages over other non-intrusive adhesive
strength measurement techniques, for instance each individual mussel can be observed and a unique detachment value can be determined for each. In addition the results from the wall jet can be used to directly estimate the values needed when using a high pressure water jet to remove zebra mussels from various materials. The variability of the results was low suggesting a high degree of consistency in the measurements.

The Preston tube provided information essential for the analysis of the wall jet data. Since the shear stress values are not uniform over the surface of the test plate, Preston tube measurements were required to provide a more accurate assessment of the nominal shear stress values at the point of mussel attachment.

The results from the adhesion strength tests showed that there was a significant difference in attachment strength among the materials tested in this study, ranging from 0.002 Pa·m² to 0.012 Pa·m² using the wall jet apparatus and ranging from 0.183 N to 1.606 N using the tensile load technique. The attachment strength of zebra mussels varied significantly with substrate type (natural ≥ metallic > polymeric), material composition and, with the roughness of the substrates. The strongest attachment occurred on macroscopically rough natural and metallic substrates (ROCK and STEEL), while the lowest attachment was measured on smooth polymeric substrates (PTFE and PMMA). There were, however, exceptions within each category. Materials of intermediate mussel attachment were less easily distinguished within the scatter of the data using either the direct (tensile loading) or the indirect (wall jet) measurement techniques. Surface roughness within a material was of importance statistically except in the case of CONC and STEEL.
The assumption that detachment is a threshold event (i.e., mussel is removed once a threshold stress is imposed on it and the detachment of the mussel is not dependent on time of exposure to the force) is reasonable.

A comparison of the two test methods indicated that the adhesion strength results from the tensile load were consistent with those from the wall jet apparatus.
Chapter 4

Measurements and Modeling of Copper Release Rates in Lake Water

4.1 Introduction

Since their introduction into the Great Lakes, the detrimental impact of zebra mussels on industry, water treatment plants, and recreational activities has been significant. New control strategies are required to reduce zebra mussel biofouling without adversely affecting the environment. Before new control strategies can be determined, a more complete understanding of zebra mussel attachment is necessary. In this work a better understanding of attachment has been gained by considering two aspects of attachment. The first aspect of attachment is the strength with which mussels attach to surfaces. The results from the studies done to determine the adhesion strength of zebra mussels were presented in Chapter 3. The second aspect of attachment is the prevention of attachment or why zebra mussels do not attach to materials. Copper was selected as the material to focus on for the investigation of this second aspect of attachment which is the topic of this Chapter.

Recruitment studies conducted in Lake Erie by the zebra mussel group at the University of Toronto (Dormon et al., 1996), and by others (Kilgour and Mackie, 1993), have shown that zebra mussels do not attach to copper and certain copper-nickel alloys. The antifouling characteristics of copper in marine environments have been known for many years and are attributed to the release of copper ions (Fingerman, 1988; Raju et al., 1988; Boyer and Gall, 1985). As discussed in Chapter 2, comparatively little information exists regarding copper release into fresh water, and it is not possible to infer a copper release rate (the amount of aqueous copper produced during copper corrosion processes) in lake water from
marine results because the behaviour of copper in fresh water differs significantly from that in sea water (Hummer, 1968).

As mentioned in Chapter 2, a number of experiments have been done to examine the behaviour of copper exposed to natural freshwater sources (Alam and Sadiq, 1989; Akkaya and Ambrose, 1987; Pisigan and Singley, 1987; Treweek et al., 1985; Hilburn, 1983; Kodama and Fujii, 1982; Brock and Popplewell, 1979; Obrecht and Quill, 1960), but the rates of copper release or corrosion differ substantially in these studies for the following reasons:

(1) the experiments were conducted using waters which had different chemistries, e.g., pH, temperature, chlorine content, hardness, conductivity and alkalinity, and

(2) analytical techniques were used which indirectly quantified copper release rates, e.g., weight loss and electrochemical measurements.

The objective of the present work was to investigate the zebra mussel antifouling mechanism of copper and to determine the potential loading of copper to the environment inherent with copper use, by measuring copper release rates in waters which were very similar to those of Lake Erie and Lake Ontario representing a large area of zebra mussel infestation.

The characterization of copper materials is presented in this work in terms of their copper release rate which provides a practical means of predicting whether a critical boundary layer concentration that will be attained under typical lake conditions. This approach was viewed as the most practical since the prediction of the actual boundary layer
concentrations from a knowledge of copper release rates would present a very challenging exercise due to the extreme variability of flow conditions that may be encountered in practice.

This Chapter describes the methods used to quantify the short term (< one month) rate of copper dissolution into lake water and proposes a model which describes the initial copper release rates under batch and continuous-flow conditions. The results from this Chapter were used to answer Objectives 4 and 5 of this thesis work, namely:

- To quantify the release rates of copper and nickel from copper and copper-nickel alloys; and
- To develop a model to predict the rate of copper release from copper and copper-nickel alloys into fresh water.

4.2 Methods and Materials

4.2.1 Copper Release Rate Studies

Copper release rate experiments were performed using both batch and continuous-flow conditions as described below.

4.2.1.1 Batch Experiments

The batch experiments were conducted in a plexiglass vessel (16 cm x 5 cm x 25 cm) lined with low-density polyethylene (LDPE) (Figure 4.1). The LDPE was added to the vessel in order to reduce copper losses due to adsorption (Moody and Lindstrom, 1977), as confirmed by preliminary experiments that showed that it had the lowest adsorption capacity
of the various materials tested, i.e., glass, plexiglass, and polytetrafluoroethylene (PTFE). For bulk water copper concentrations of 1.0 mg L\(^{-1}\), approximately 5 - 8% of the copper in the above vessels adsorbed to the LDPE liner. The vessel was held on a shaker table (Gyrotary Water Bath Shaker, New Brunswick Scientific, Edison, New Jersey) and gently agitated in order to have well-mixed conditions within the vessel. Four slotted PTFE\(^1\) bars were used to hold the copper plates upright in the vessel. Each vessel held four copper plates having dimensions of 8 cm x 15.5 cm x 0.16 cm. An air pump connected to LDPE tubing was used to maintain saturated oxygen concentrations within the vessel. The vessel was wrapped with aluminum foil to avoid changing light conditions which can affect oxide layer formation (Kruger, 1959), and was covered in order to prevent evaporative water loss.

\(^1\) The holding pieces could not be made from LDPE hence PTFE was the best alternative.
Figure 4.1: Experimental Set-up for Batch and Continuous-Flow Conditions
The batch studies were performed in a series of experiments depicted in Table 4.1 which shows the combinations of materials and water conditions used to measure copper release rates, specifically: acid-etched copper (procedure described below) in fresh lake water, aged copper in fresh water, and etched copper in aged water. Water collection for the various experiments was conducted throughout the study. The first batch experiment (etched copper in fresh water) was done to determine the change in bulk water copper concentration with time, and the remaining experiments, the "double exposure experiments", were performed in order to further elucidate the trends observed under batch conditions. The protocols for these experiments are described in more detail below.

In the first of the seven batch experiments, four copper alloy plates (C110)\(^2\), (8 cm x 15.5 cm x 0.16 cm) were acid-etched using a sulphuric-nitric acid dip (1 part sulphuric acid:1 part nitric acid:1 part water; Snogren, 1974) in order to achieve a uniform initial surface condition. The plates were rinsed with cold tap water and distilled water and then allowed to dry. The four copper plates were placed into the PTFE holders described above and 1 L of filtered (0.2 mm nominal) Lake Ontario water was added to the vessel. Water from Lake Ontario had essentially the same composition as that from the Lake Erie zebra mussel test site, as shown in Table 4.2 (represents an average water quality for all lake water used in all of the release rate experiments). Temperature and pH were monitored throughout the duration of the experiment (pH = 8.17 ± 0.08, temperature = 22 ± 1 °C, additional parameters

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\(^2\) Copper Development Association (CDA) numbering convention.
### Table 4.1: Description of Copper Batch Experiments

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Conditions</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1. Four copper plates 2. Acid etched 3. 1 L fresh, filtered lake water 4. One week duration</td>
<td>To quantify the copper release rate from copper plates into lake water.</td>
</tr>
<tr>
<td>2</td>
<td>1. Four copper plates 2. Acid etched 3. 1 L fresh, filtered lake water 4. One week duration</td>
<td>To determine whether the copper release rate/copper concentration changes after longer exposure periods.</td>
</tr>
<tr>
<td>3</td>
<td>1. Four copper plates 2. Acid etched 3. 1 L fresh, filtered lake water 4. One week duration 5. Same copper plates (conditioned for one week) 6. 1 L fresh, filtered lake water 7. One week duration (total duration - 2 weeks)</td>
<td>To determine whether the copper release curve observed in the batch experiments is the result of passivation or the build up of copper in the bulk solution.</td>
</tr>
<tr>
<td>4</td>
<td>Same protocol as Experiment 3, except: 1. Conditioned copper plates (four) were rinsed twice with fresh, filtered lake water 2. 1 L fresh, filtered lake water 3. One week duration (total duration - 2 weeks)</td>
<td>To determine the cause of the initial burst of copper concentration in Experiment 3</td>
</tr>
<tr>
<td>5</td>
<td>1. Two week lake water conditioned copper plates (four) 2. Copper-containing lake water (1 mg/L) which had been flushed out (continuous flow) with fresh, filtered lake water for 48 hours to reduce copper concentration to a level similar to lake water 3. System converted back to batch conditions</td>
<td>To confirm the results from Experiments 3 and 4. Specifically, to determine whether exposure to air, between experiments, influenced the copper surface.</td>
</tr>
<tr>
<td>6</td>
<td>1. Four copper plates 2. Acid etched 3. 1 L high copper concentration lake water (0.8 - 0.9 mg/L) 4. One week duration</td>
<td>To isolate the effect of bulk water copper concentration.</td>
</tr>
<tr>
<td>7</td>
<td>1. Copper plates 2. At completion of one month duration batch experiment 3. Sample times of T=0, 72 hours and 1 month 4. Examined using XPS</td>
<td>To determine whether the change in copper surface corresponds to the batch experimental profile.</td>
</tr>
</tbody>
</table>

* All lake water was filtered (0.2 mm nominal) prior to use in the experiments
given in Table 4.2). Water samples were extracted from the middle of the vessel at regular
time intervals, acidified to a pH < 2 using environmental grade nitric acid (EPA, 1990), and
analyzed for copper content using graphite furnace atomic absorption spectrometry (GFAAS;
SpectraAA, Varian; detection limit of 0.4 mg*L\(^{-1}\)). The experiments were conducted for two
time periods: one week (first batch experiment) and one month (second batch experiment).

In the third batch experiment, four acid-etched copper plates were placed into 1 L of
filtered Lake Ontario water, as described above, for one week. At the end of the week, the
plates were removed from the vessel and placed into a new vessel containing 1 L of fresh
lake water. The experiment was terminated at the end of the second week. This type of batch
experiment is referred to as a "double-exposure" experiment. The results from this
experiment showed that there was an initial increase in copper concentration when the plates
were placed into the second vessel. In order to determine the cause of the increase in copper
concentration, a fourth batch experiment was performed. This experiment was similar to the
second batch experiment except that the plates were rinsed twice in lake water prior to
placing the plates into the vessel for the second exposure period. Temperature and pH were
monitored throughout the duration of the experiment (temperature = 20 \(\pm\) 3 \(^\circ\)C, pH =
8.17 \(\pm\) 0.8). Water samples were taken at regular time intervals during both weeks and
analyzed as above. The goal was to investigate the role of oxide growth on the copper
release.

The fifth batch experiment was a continuation of the second. The copper-containing
bulk water remaining from the second double-exposure period was flushed out with fresh,
filtered lake water for 48 hours to reduce the copper concentration within the vessel to a level similar to lake water conditions. Once the copper concentration had been reduced, the system was returned to batch conditions and the change in copper concentration was monitored by taking samples at regular time intervals. This experiment was done to confirm the results from the second and third batch experiments using a protocol that did not expose the copper plates to air between batch periods.

In the sixth batch experiment, acid-etched copper plates were placed into the copper-containing bulk lake water (having a copper concentration of 0.8 - 0.9 mg\textbullet{}L\textsuperscript{-1} ) remaining from the fourth batch experiment described above and held under batch conditions. The copper concentration was monitored with time and compared to the results obtained from the earlier experiments. The goal was to isolate the effect of bulk-water copper concentration.

In the seventh batch experiment, the surfaces of the copper samples from the batch experiments were analyzed using X-ray photoelectron spectroscopy (XPS). Copper samples were removed from the batch vessels at times of \( t = 0 \) (freshly acid-etched surface), \( t = 72 \) hours and \( t = \) one month which represented different copper release along the batch profiles. The samples were cut to the appropriate size and then analyzed by Dr. T. Debies from Xerox, Webster, New York. The XPS analytical method is described in Appendix C.
Table 4.2: Comparison Between Lake Erie Water and Lake Ontario Water*

<table>
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<td>LangIndex</td>
<td>0.4</td>
<td>.488/.323</td>
<td>0.461</td>
<td>.650/.413</td>
</tr>
<tr>
<td>Mg(mg/L)</td>
<td>9.12</td>
<td>9.5/8.7</td>
<td>8.5</td>
<td>8.95/8.3</td>
</tr>
<tr>
<td>Cu(ug/L)</td>
<td>2.49</td>
<td>3.6/1.6</td>
<td>18.22</td>
<td>36.93</td>
</tr>
</tbody>
</table>

*All of the data is from treatment plant raw water.


4.2.1.2 Continuous-Flow Experiments

The batch experimental set-up, as described above, was modified to include inflow and outflow ports (Figure 4.1). A constant flow of filtered Lake Ontario water was provided by a peristaltic pump (Masterflex) and water flow rates were determined at each sampling time by measuring the time to fill a volumetric flask. The vessel was agitated on the shaker table as in the batch experiments.

Two types of experiments were conducted using the continuous-flow set-up (see Table 4.3). The first experiments were performed to establish the range of flow rates above which the copper release rate was independent of the flow rate. The second set of experiments examined the effects of a wider range of mass transfer coefficients on the copper release rate in order to determine whether or not continuous-flow conditions corresponded to the reaction-limited regime as described in the model (discussed following the results section).

In the first set of continuous-flow experiments, four acid-etched copper plates (C110) were conditioned in aerated, filtered Lake Ontario water for 48 hours under dark conditions prior to being placed into 1 L of filtered Lake Ontario water in the continuous-flow set-up. The continuous-flow experiments were conducted at flow rates of 2, 8, 16, and 32 mL·min⁻¹. There were two limitations which prevented continuous testing at flow rates greater than 32 mL·min⁻¹: (1) the copper concentration in the bulk water at higher flow rates would be below the detection limit of GFAAS; and (2) the quantity of water required to conduct the experiments was not practical under laboratory conditions. Temperature and pH were
Table 4.3: Description of Copper Continuous-Flow Experiments

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>Conditions</th>
<th>Purpose</th>
</tr>
</thead>
</table>
| 1                 | 1. Four copper plates  
2. Acid etched  
3. Conditioned in fresh, filtered, aerated lake water for 48 hours, under dark conditions  
4. 1 L fresh, filtered lake water  
5. Flows of 2, 8, 16 and 32 mL/min  
6. Continued until copper concentration achieved a steady-state. | To establish the range of flow rates above which the copper release rate was independent of flow rate. |
| 2                 | 1. Four copper plates  
2. Acid etched  
3. Conditioned in fresh, filtered, aerated lake water for 48 hours, under dark conditions  
4. 1 L fresh, filtered lake water  
5. Flow rate of 10 mL/min  
6. System allowed to reach steady-state (after 7 days)  
7. Propeller placed into vessel and ran at speeds of 45, 300 and 500 rpm for 48 hours  
8. Propeller removed  
9. Vessel agitated on shaker table for 72 hours. | To examine the effects of a wider range of mass transfer coefficients to determine whether copper release rate was reaction limited or mass transfer limited. |

* All lake water was filtered (0.2 mm nominal) prior to use in the experiments
monitored throughout the duration of the experiment (temperature = 21 ± 2 °C, pH = 8.2 ± 0.8). Water samples were taken from the bulk solution at the outlet port of the vessel at regular time intervals, acidified to a pH < 2 using environmental grade nitric acid and analyzed using GFAAS.

In the second set of continuous-flow experiments, an LDPE propeller stirrer was placed in the vessel and operated at 45, 300 and 500 rpm with the shaker table turned off. The latter two speeds were selected to provide much greater mass transfer rates in the vessel compared to the shaker table alone. Stirring speeds were kept below 500 rpm because greater speeds caused excessive air entrainment. Initially, four acid-etched copper plates were conditioned in aerated, filtered Lake Ontario water for 48 hours under dark conditions prior to being placed into 1 L of filtered Lake Ontario water in the continuous-flow experimental set-up at a flow rate of 10 mL min⁻¹ and allowed to reach steady-state (approximately seven days). The stirrer was then introduced into the vessel at the highest speed (500 rpm) for 48 hours and then the stirrer speed was reduced to 300 rpm for another 48 hours. A second experiment was conducted under the same conditions except that once steady-state had been achieved (after seven days) the stirrer was introduced into the vessel and was operated at a speed of 45 rpm for 48 hours. In both experiments, after the stirrer was removed the vessel was again agitated on the shaker table for 72 hours. Temperature and pH were monitored throughout the duration of the experiment (pH = 8.2 ± 0.8, temperature = 21 ± 2 °C). Water samples were taken from the bulk solution at the outlet port of the vessel at regular time
Chapter 4: Measurements and Modeling of Copper Release Rates in Lake Water

intervals and analyzed as before.

Water velocity measurements were performed to estimate the difference in stirring rates under high-speed stirred conditions compared to agitated conditions (shaker table alone). Neutrally buoyant particles of acrylonitrile-butadiene-styrene (ABS) ($\rho = 1000 \text{ kg m}^{-3}$, diameter $< 2 \text{ mm}$) were added to the vessel and their velocities were measured using a video recorder. Velocity measurements were made on particles moving vertically between the plates in the vessel by replaying the videotape in slow motion.

4.3 Results

4.3.1 Batch Experiments

The results from the first batch experiment are shown in Figure 4.2 as the change in copper concentration with time. Initially, there was a rapid increase in copper concentration but this curved sharply to a plateau at approximately 1.2 mg L$^{-1}$ which was maintained for almost 100 hours. This trend was investigated further using a series of "double-exposure" experiments in order to determine whether the transition to the plateau part of the curve at 1.2 mg L$^{-1}$ resulted from the build-up of an oxide layer on the copper surface or from the increasing bulk copper concentration.

The two concentration curves from the second and third batch experiments ("double-exposure") using aged copper in fresh lake water (Figures 4.3 and 4.4) are almost identical which indicates that the build-up of copper within the vessel influences the copper release rate. The results from the fifth and sixth batch experiments are shown in Figure 4.5 for the
Chapter 4: Measurements and Modeling of Copper Release Rates in Lake Water

Figure 4.2: Release curve from copper batch experiment.
Figure 4.3: Release curves from the double-exposure experiments comparing the two exposure periods under batch conditions. (Error bars are the standard errors of replicate results ($n=2$) from the analysis of each water sample).
Figure 4.4: Release curves from the second double-exposure experiment comparing the two exposure periods under batch conditions. [Note the increase in copper concentration when the copper plates are placed into the vessel for the second exposure period.] (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
entire period of the experiments. Figure 4.5 shows a decrease in copper concentration from approximately 0.7 mg*L⁻¹ to 0.3 mg*L⁻¹ through dilution by flushing with Lake Ontario water (up to time = 48 hours). The copper concentration in the bulk water then increased rapidly to approximately 1.1 mg*L⁻¹ and after 400 hours under batch conditions the copper concentration decreased to 0.9 mg*L⁻¹. The water remaining from this experiment was used with freshly acid-etched copper in the seventh batch experiment which began at time = 680 hours (where t = 0 was the beginning of the fifth batch experiment), as shown in Figure 4.6.

In the seventh batch experiment (Figure 4.6; beginning at t = 680 hours), the copper concentration initially decreased to approximately 0.55 mg*L⁻¹ and then increased rapidly to a value of 1.0 mg*L⁻¹. The concentration did not remain at the plateau value for as long as observed in previous batch experiments but instead decreased gradually to 0.8 mg*L⁻¹ after approximately 100 hours of exposure. A comparison of the results from the three double-exposure experiments show that similar copper concentration trends; rapid concentration increase levelling to a plateau region, are obtained from the different surface treatments and water copper concentrations. These results confirm that the decrease in initial release rate is due to the build-up of copper concentration in the vessel rather than passivation of the copper surface from the growing copper oxide layer.

At the completion of the seventh batch experiment it was noted that there was a considerable amount of copper blue-green precipitate present at the bottom of the test vessel and on the copper plates. At the end of the experiment, the remaining bulk liquid was thoroughly mixed with the precipitates and acidified to a pH < 2 for analysis by GFAAS.
Figure 4.5: Continuum of release curves for the remaining double exposure curves; specifically the continuous flushing out of the water from the long-term batch experiment for the start of the experiment using aged copper in fresh lake water. The water remaining from this experiment was used for the etched copper in aged water experiment. Error bars are the standard errors of replicate results (n = 2) from the analysis of each water sample.
Chapter 4: Measurements and Modeling of Copper Release Rates in Lake Water

The results showed that the copper concentration was then 3.0 mg·L⁻¹, as opposed to 0.8 mg·L⁻¹ in the bulk water prior to the mixing of the precipitates. This suggests that precipitation is occurring within the vessel under batch conditions. Long term batch experiments were conducted for one month in order to observe how the copper concentration in the bulk solution changed beyond the initial release rate. When the exposure period of the batch experiment was extended, the copper concentration gradually decreased (at a rate ≈ 0.7 μg·L⁻¹·h⁻¹) to 0.7 mg·L⁻¹ after 750 hours (Figure 4.6).

The XPS analysis showed that the oxide on the initial acid-etched copper surface (t=0) consisted mostly of Cu₂O (65 %) with the remainder being Cu(OH)₂. After 72 hours of batch exposure, the copper surface had both shiny and green patches. The shiny surface was found to contain Cu(OH)₂ (56 %), CuO (28 %), with the remainder being mostly metallic copper. The thick green oxide patches contained only Cu(OH)₂. Finally, the copper surfaces which had been conditioned in lake water for more than 30 days were also analyzed and found to be composed of CuO (40 %), Cu₂O (35 %), and Cu(OH)₂ (25 %).

4.3.2 Continuous-Flow Experiments

The results from the first set of continuous-flow experiments, conducted at different flow rates (including replicates), are shown in Figure 4.7. As expected, the trend in copper concentration differs considerably from the typical curve obtained in the batch experiments (Figure 4.2) and is a function of the flow rate through the vessel. Under continuous-flow conditions, the copper concentration within each vessel initially increased rapidly and then...
Figure 4.6: Long-term batch experiments showing the decrease in copper concentration from the plateau region after longer exposure times. Error bars are the standard errors of replicate results (n = 2) from the analysis of each water sample.
Figure 4.7: Comparison of the change in copper concentration under continuous-flow conditions at various flow rates including repeat experiments. (See Table 5.3 for data confidence intervals).
became approximately constant after about 80 hours and the copper concentration at steady-state decreased with increasing flow rates. The higher flows (> 8 mL•min⁻¹) had lower concentrations that were inversely proportional to the flow rate, i.e., doubling the flow rate, decreased the concentration by approximately half, thereby producing the same copper release rate.

The copper concentration data obtained under continuous-flow conditions were repeatable. This can be observed by considering the concentration values at 8 mL•min⁻¹ conducted in two different experiments (Figure 4.7). In the first experiment, the flow rate of 8 mL•min⁻¹ corresponded to a steady-state copper concentration of 208 µg•L⁻¹ and for another experiment at a flow rate of 8 mL•min⁻¹ the steady-state copper concentrations were 206 µg•L⁻¹ and 202 µg•L⁻¹ for replicate experiments.

Data for the second set of continuous-flow experiments under stirred conditions are shown in Figure 4.8 as an effective copper release rate, calculated by multiplying concentration and flow rate and then dividing the result by the surface area of the copper plates. Stirring at 45 rpm did not change the steady-state copper release rate obtained under agitated conditions (using the shaker table alone) (Figure 4.8). High-speed stirring at 300 and 500 rpm increased the copper release rate slightly from the steady-state value under agitated conditions (Figure 4.9). In all cases, the copper release rate returned to the initial steady-state value when the vessel was placed again under agitated conditions (shaker table alone). The water velocity measurements showed that under high-speed stirred conditions (500 and 300
rpm) the average velocity in the vessel was approximately 4 cm s⁻¹, which was ten times greater than the velocity found under low-speed stirring (45 rpm) and agitated conditions. These velocities are consistent with the expectation that increasing the stirring speed by a factor of ten would cause a similar increase in velocity. At 4 cm s⁻¹, the plate spacing of 8 mm gives rise to a Reynolds number, Re = 763 (500 rpm) and 460 (300 rpm), indicating a laminar flow in that region.
Figure 4.8: Evaluation of mass transfer effects on the release of copper under stirred conditions at a speed of 45 rpm compared to agitated (shaker table) conditions.
Figure 4.9: Evaluation of mass transfer effects on the release of copper under stirred conditions at speeds of 300 and 500 rpm compared to agitated (shaker table) conditions. Error bars are the sum of the errors associated with the calculation of release rate, i.e., concentration measurement error, flow rate measurement error and area measurement error.
4.4 Copper Release Rate Model

The dissolution rate of copper in a freshwater environment was modeled to describe the observed behaviour under both batch and continuous-flow conditions. It is postulated that there are four major processes occurring in parallel when copper corrodes in fresh water:

(i) dissolution;
(ii) mass transfer;
(iii) precipitation; and
(iv) passivation.

The first process is the dissolution of copper into water. This process is referred to as the “reaction mechanism” which, for the purposes of the model, combines both the kinetics of copper corrosion and the diffusion of copper ions through the growing oxide layer. These were combined because the goal of this study was to determine the initial total release rate from a copper surface into bulk solution rather than to investigate the details of corrosion kinetics and ion diffusion.

The second process involves a mass transfer mechanism in which the reaction products move away from the copper solid-water interface into the bulk lake water.

The third process is the precipitation of copper species from solution. Precipitation occurs once the bulk copper concentration reaches the solubility limit of the copper compounds or reaches a supersaturated concentration within solution which initiates precipitation. The driving force for precipitation is the difference between the solubility limit of the copper species and the bulk copper concentration in the water. As the copper
concentration in the bulk water increases, the driving force for precipitation increases.

The fourth process is the build-up of a copper-containing layer or passivation of the copper surface which decreases the amount of copper released. The copper surface builds up a copper-containing layer and/or passivates under the combination of the corrosion mechanism and the precipitation of copper species from solution onto the metal plates. Passivation occurs when the metal is oxidized to an oxide that is stable in the electrolyte (Scully, 1975). As the copper surface begins to passivate, the dissolution rate of copper into water decreases. These processes, at times, act simultaneously to control the release of copper into solution under batch conditions, some dominating at different stages.

These processes are noticeable throughout all of the batch experiments in which there is a rapid increase in copper concentration up to a maximum (supersaturation) followed by a plateau and then a decrease with time to a constant value. Initially the copper release rate is dominated by copper dissolution into water which results in a linear relationship between copper concentration and time. However, as the copper concentration in the vessel continues to increase, mass transfer processes slow the release of copper into solution because the electrochemical potential (E) of the metal becomes more noble as copper concentration increases, slowing down the dissolution reaction (Scully, 1975). At the same time, the solubilities of copper species are surpassed and a supersaturation point is achieved, causing copper species to precipitate from solution, thereby decreasing the soluble copper concentration. Finally, the copper surface begins to build up a copper oxide layer (passivation layer) resulting from both corrosion reactions at the surface and nucleation and precipitation
of copper species from solution which further slows down the dissolution rate. Therefore, at all points along the batch release curve there are four processes occurring simultaneously with individual processes or combinations of processes dominating the copper release rate at various times.

Combining these processes into a mass balance around the copper surface under batch conditions (Figure 4.10), assuming pseudo-steady-state conditions, results in the following equation describing the copper concentration in bulk water:

\[
\text{copper accumulation in bulk water} = \text{reaction and mass transfer from copper surface into bulk water} - \text{precipitation} \quad (4.1)
\]

Passivation does not appear formally in the equation because in the mass balance around the copper surface, the passivation mechanism slows the reaction rate by forming an oxide on the surface of the copper. This is interpreted in the mass balance as a reduction in reaction rate.

Since several processes are occurring in solution simultaneously at higher concentrations it is difficult to identify the individual rates of these processes. However, the goal of this thesis is to model the rate of copper release from a copper surface into a freshwater environment having a copper concentration very much lower than the supersaturated condition and so it can be assumed that only the reaction process is significant i.e., the kinetics of copper corrosion and diffusion of copper ions through the oxide layer is significant. Since the other processes are dependent upon the bulk copper concentration in
the vessel, these processes were assumed to be negligible under freshwater conditions (i.e., low copper concentration).

Figure 4.10: Simplified view of processes occurring at the copper surface resulting in the release of copper from a solid surface, Cu(s).
When copper corrodes in freshwater the following reactions can occur:

1. \( \text{Cu} \rightarrow \text{Cu}^{+} + e \)
2. \( \text{Cu} \rightarrow \text{Cu}^{2+} + 2e \)
3. \( \text{Cu} + \text{Cu}^{2+} \rightarrow 2 \text{Cu}^{+} \)
4. \( 2\text{Cu}^{+}_{(aq)} + \frac{1}{2} \text{O}_{2} + 2 \text{H}^{+} \rightarrow 2 \text{Cu}^{2+} + \text{H}_{2}\text{O} \) (in solution)
5. \( 3\text{Cu}^{2+} + 2\text{H}_{2}\text{O} \leftrightarrow \text{Cu(OH)}_{2(s)} + 2\text{H}^{+} \)

Equations (1) through (4) occur under the reaction mechanism of copper release. Equation (5) represents a precipitation reaction and is presented only to illustrate the type of reactions that can occur when copper reacts with freshwater.

The conversion of solid copper to aqueous copper (i.e., a combination of Equations (1) - (4)) is represented, for modelling purposes as,

\[ \text{Cu} (s) \rightarrow \text{Cu} (aq) \quad (4.2) \]

which occurs through corrosion reactions and diffusion through the oxide (the "reaction mechanism").

### 4.4.1 Batch Release Rate Model

Considering a batch corrosion experiment in a closed vessel containing water having volume, \( V \), the copper dissolution is dependent upon the following reaction equation:

\[ V \frac{d \text{Cu}_b}{dt} = rA \quad (4.3) \]
where \( C_{ui} \) is the copper concentration at the copper-water interface, \( C_{ub} \) is the bulk water copper concentration, \( V \) is the volume of solution, \( A \) is the surface area of the copper in the vessel, \( r \) is the reaction rate and it is assumed that \( r \) does not change over the low bulk copper concentrations. Integration of Equation (4.3) yields:

\[
C_{ub} = \left( \frac{r}{V} \right) I_i
\]  

(4.4)

Equation (4.4) represents a linear model for copper release from time \( t = 0 \) to a time \( t = t_i \), where \( t_i \) is some time before the other processes (ii-iv, page 65) begin to dominate.

4.4.2 Continuous-Flow Release Rate Model

Continuous-flow conditions are different from batch conditions because there is a constant introduction of fresh water and an extraction of reaction products from the vessel. A schematic diagram of the continuous-flow conditions is shown in Figure 4.1, where \( F \) is the volumetric flow rate (volume/time) into and out of the vessel, \( C_{ui} \) is the inlet concentration of copper in lake water and \( C_{ub} \) is the bulk lake water copper concentration in the outlet stream. The results from the stirred vessel experiments indicated that the processes occurring under continuous-flow conditions were reaction limited, i.e., only process (i) (page 65) was significant. Therefore, only the reaction rate was considered in the following model.

The copper mass balance for the bulk water is:
Chapter 4: Measurements and Modeling of Copper Release Rates in Lake Water

where $A$ is the surface area of copper exposed to lake water, and it is assumed that the vessel is sufficiently mixed so that there is a uniform $Cu_b$ throughout the vessel. If the continuous-flow system reaches a steady-state, i.e.,

$$
\frac{d\ Cu_b}{dt} = 0
$$

Equation (4.5) becomes:

$$
F(Cu_n - Cu_b) = -r \ A
$$

Rearranging this equation to solve for $r$ yields:

$$
r = \frac{F(Cu_b - Cu_n)}{A}
$$

The copper release rate, $r$, can be easily obtained by substituting the steady-state flow rate and copper concentrations into Equation (4.8).

Equation (4.4) is the model for batch copper release rates under the reaction-limited
regime. Equation (4.8) describes the copper release rate for continuous-flow experiments under reaction-limited regimes. These models were evaluated using the results from the copper release rate experiments which were conducted in Lake Ontario water.
4.5 Discussion

4.5.1 Batch Experimental Profiles

Figure 4.2 shows that the change in copper concentration with time under batch conditions followed a typical trend consisting of a rapid increase followed by a relatively sharp transition to a plateau concentration as time increased, and that this trend was repeated upon a second exposure. This behaviour is qualitatively explained by the model which predicts that the release rate of copper is approximately constant at low copper concentrations (in the reaction-limited regime) and then decreases with increasing copper concentration as the precipitation, mass transfer rate of copper from the interface into the bulk water and copper surface passivation become important.

The apparent decline in copper concentration (Figure 4.3 and 4.4) along with the decline in release rate during the continuous-flow experiments (Figure 4.5) prompted the closer examination of the batch process through the series of double-exposure experiments (batch experiments 2-5). The effect of air exposure on the copper release rate in the double-exposure experiments during the transfer to the new vessel was initially examined by performing the same test in two different ways. Using the first method, aged copper plates were removed from the aged water and placed into a new vessel containing fresh lake water. The second method avoided air exposure by gradually flushing out the aged copper solution with fresh lake water while the aged copper plates remained in the vessel. The data were similar for both methods indicating that air exposure did not affect the copper surfaces during the transfer to the new test vessel.
The results from the double-exposure experiments supported the hypothesis that the decreasing copper release rate under batch experimental conditions was due to the increasing copper concentration within the vessel rather than the result of passivation of the surface alone at the first plateau level. If the latter was the case, the second concentration curve in the double-exposure experiments should be substantially lower due to a suppressed release of copper, but in every case the second exposure curve attained similar copper concentration profiles with time.

The results from the batch double-exposure experiments may be explained by considering the events that occur when copper is initially placed into lake water. Under batch conditions, metal dissolution initially occurs and over time, a high copper concentration in the bulk solution is attained representing a supersaturated concentration, as described by the model. During this time, copper species precipitate from solution allowing a loosely-adherent copper-rich layer to form on the surface of the copper plates, and when these copper surfaces are again placed into fresh lake water (a new non-equilibrium condition), the layer formed in the first exposure period dissolves rapidly in this new solution. This process is illustrated by the data of Figure 4.3 from the second batch experiment.

In the second batch experiment, aged copper plates from the first exposure period were placed into fresh lake water for a second exposure period and a slight increase in the release rate of copper was observed approximately one hour after placing the copper plates into fresh lake water (Figure 4.2). A third batch experiment (double-exposure) was conducted to determine the cause of the elevated copper release rate during the initial stages
of the second exposure. The same method that was used in the first double-exposure experiment was repeated except that prior to placing the exposed plates directly into the second fresh lake water solution, the copper plates were rinsed twice by placing them into lake water in an LDPE bag and agitating the water in order to remove the copper-rich layer on the surface. The results from this experiment showed that the slight initial increase in copper concentration did not occur after the copper plates had been rinsed, thus supporting the hypothesis that the initial high copper release rate was due to the presence of a copper-rich layer on the copper plates after the first week of batch exposure. The rapid dissolution of the copper-rich layer allows the surface to corrode again resulting in a trend which is similar to the first exposure curve. This trend was observed in each of the double-exposure experiments indicating that the results observed were not due to surface effects. The formation of a copper-rich layer on the surface is consistent with the hypothesis that precipitation and nucleation events are occurring on the surface which is a result of the supersaturated copper solution within the vessel. The occurrence of the precipitation and nucleation reactions are also supported by the presence of precipitates on the copper surface and on the bottom of the vessel.

In order to further explore this phenomena, the acid-etched copper in aged water experiment (fifth batch experiment) was a different approach to the double-exposure experiments, but the results show that under batch conditions, the system first adjusts to the new conditions imposed by the addition of the etched copper plates and then a similar copper concentration versus time trend is observed.
Overall, these double exposure experiments confirm the hypothesis, upon which the model is based, that the build-up of copper concentration in the solution under batch conditions affects the release rate of copper. This suggests that batch experiments may not provide the best means for accurately quantifying the copper release rate into a lake water environment since they allow a build-up of copper concentration in the bulk solution. Lake water has a very low background copper level (i.e., well below the saturated copper concentration) and therefore copper release tends to be in the reaction-limited regime.

Long-term batch experiments (second batch experiment) were performed for one month to determine whether the copper concentration plateau region represented a true equilibrium condition. The initial copper concentration trend was similar to the short-term experimental results, however, when the exposure time was extended to one month (Figure 4.6) the copper concentration decreased from the plateau value to approximately 0.7 mg*L⁻¹ after a period of 750 hours. This drop in copper concentration under batch conditions suggests that 1.1 mg*L⁻¹ was not the final equilibrium value but rather represented a supersaturated condition, considerably above the solubility values given in Chapter 2, i.e., CuCO₃ - 0.3 mg*L⁻¹. Such a supersaturated state can be understood from some past studies reported in literature.

The dissolution and oxidation of copper has been studied in various alkaline solutions, such as LiOH and NaHCO₃, using electrochemical techniques under anodic conditions (Drogowska et al., 1993; 1992a,b; Shoesmith et al., 1983; 1976; El-Tantawy et al., 1981; Ashworth and Fairhurst, 1977; Ambrose et al., 1973). These studies suggest that once
the solution close to the copper surface becomes supersaturated with copper, then nucleation and growth (precipitation) of copper species occurs from solution. Edwards et al. (1996) referred to a set of empirical relationships, which are functions of alkalinity and pH, used to predict the maximum concentration of copper release to water during stagnation. If the present test conditions are substituted into the equation for a new copper pipe, the maximum copper concentration predicted is 0.68 mg*L$^{-1}$ which is lower than the plateau copper concentration obtained for the present batch experiments (1.0 mg*L$^{-1}$) but very close to the final value of 0.7 mg*L$^{-1}$. The existence of a supersaturated condition provides an explanation for the initial plateau at 1.0 mg*L$^{-1}$, with decrease in copper concentration resulting from precipitation.

Other studies have also observed the precipitation of copper from a supersaturated copper solution. Two different mechanisms reducing the copper concentration in solution were postulated. The first was presented by Ashworth and Fairhurst (1977) who suggested that once Cu$_2$O formed, only saturation was required for the growth of the Cu$_2$O nuclei allowing the copper concentration to decrease to a lower value. Alternatively, Armstrong (1971) stated that once precipitation occurred, the precipitate formed close to the copper surface, decreasing the metal dissolution reaction.

In the present study both a reduction in copper concentration in solution (i.e., decrease in metal dissolution reaction) and precipitation were observed. The copper concentration decreased to 0.7 mg*L$^{-1}$ which is the predicted saturated copper concentration in water suggested by Edwards (1996). At the same time, there was also a thick, green precipitate
present on the surfaces of the copper plates (as indicated by XPS studies) and at the bottom of the test vessel. Although the exact mechanism cannot be determined from the experiments conducted in this work, the consistent rise in copper concentration to a supersaturated concentration which was larger than the maximum predicted copper concentration under stagnant conditions, and the presence of precipitate on the copper surfaces and at the bottom of the test vessel agree with the results from previous studies and therefore the mechanism may be a combination of the two proposed theories. Again, these results suggest that batch experiments do not provide an accurate assessment of the copper release rate in fresh lake water because the rate is affected by the build-up of copper in the bulk solution. This result is significant because batch studies are commonly used to quantify metal release or dissolution rates into aqueous media. The present work implies that such experiments may actually underestimate the release rate of the metal into solution due to the high metal concentrations suppressing further dissolution.

The differences in the oxide species formed on the copper surfaces over time were not consistent. This may be explained by the non-uniformity of the precipitation of the oxide on the surface (indicated by the visible shiny and green patches present after 72 hours), the different sample locations used for the analysis, and the loss of loosely adherent precipitate from the surface when the samples were taken from the water. However, the XPS analysis showed that the green precipitate on the copper plates was Cu(OH)$_2$ which formed after 72 hours, and after 30 days three oxide species were present on the surface: Cu$_2$O, Cu(OH)$_2$ and CuO. These results agree with the reported literature; namely, after the supersaturated copper
level is reached under batch conditions, the copper concentration decreases as CuO forms (Shoesmith et al., 1975).

An alternate approach to understanding the batch experimental results considers the reaction species in solution and their effect on the release rate. Under different environmental conditions, either Cu\textsuperscript{2+} or Cu\textsuperscript{+} will be present in aqueous solutions. Examining the electrode potentials for the equilibria reactions of these species, namely,

\begin{align*}
\text{Cu}^{2+} + 2e & \rightarrow \text{Cu} & E^\circ(V) = +0.34 \\
\text{Cu}^+ + e & \rightarrow \text{Cu} & E^\circ(V) = +0.52
\end{align*}

indicates that cupric ions (Cu\textsuperscript{2+}) dominate over cuprous ions. However, this is not true for very dilute solutions. Cupric ions are normally stable but become unstable when the cuprous ions concentration is very low (Scully, 1975). In addition, the presence of oxygen in solution can affect the speciation of copper in solution. Oxygen acts as an electron acceptor, resulting in the formation of Cu\textsuperscript{2+} (Scully, 1975). The dynamics between the two valences of copper also affects the copper release rate. Evidence of both species can be found by observing the oxide species present on the copper surface.

It has been noted that the lifetime of the cuprous ion in water is usually very short (<1 second) indicating that it is quite unstable (Uhlig, 1963) and as stated above, only occurs in dilute solutions. Therefore, the dominance of either species can change throughout the
duration of the experiment and may impact on the copper batch rate at various points along the release rate curve.

In summary, the combination of the batch experimental XPS results, the decrease in copper concentration and formation of precipitates result in the same explanation for the experimental results as suggested by the literature. Under batch conditions, the bulk copper concentration increases to a supersaturated condition (approximately 1.1 mg·L⁻¹) followed by precipitation and passivation of the copper surface over time, resulting in a reduction in copper release rate.

4.5.2 Batch Model Parameters

The results from the first double exposure experiment were used to examine the proposed model for its ability to predict the initial release rate of copper under batch conditions. The batch release curve can be divided into four regions (Figure 4.11): the first region is the reaction-limited regime; the second region represents the beginning of the precipitation reaction regime; the third region is a mixed regime consisting of comparable dissolution, precipitation, passivation and mass transfer-limited rates; and the last region is one in which the (supersaturation) concentration decreases due to precipitation while dissolution continues at a reduced rate because copper surface slowly becomes passivated until a steady-state copper concentration is attained.

The values from the reaction-limited section of the curve (far below the saturated concentration) were used to solve for the reaction rate constant, r, by plotting bulk copper concentration versus time, where the slope of the line is:
As shown in Table 4.4, the reaction rate constants were very similar for the two double-exposure experiments, although the value of $r$ depends on the time chosen to represent the end of the reaction-limited regime. Therefore, there is significant uncertainty associated with the calculation of the initial slope of the batch concentration curve for determining the initial copper release rate into natural lake water (zero bulk copper concentration).

Although this model describes the initial release rate of copper into lake water under batch conditions, it does not describe the decrease in copper concentration from the supersaturation copper concentration due to precipitation, mass transfer and passivation which are far too complex to model. In order to include the other processes occurring in the vessel under batch conditions, further kinetic studies would have to be completed for a better understanding of the dissolution, precipitation and passivation rates. However, the principal objective of this study was to measure and model the copper release rate into lake water, and therefore the model satisfies the present requirements.
Figure 4.11: The batch-conditions model as applied to the double exposure experimental results. The curve is divided into the four regions hypothesized in the model. Error bars are the standard errors of replicate results (n = 2) from the analysis of each water sample.
4.5.3 Continuous-Flow Experimental Profiles

The continuous-flow experiments were designed to more accurately quantify the release rate of copper from copper sheet into fresh water. Since the flow through the vessel was continuous, the system could be operated so that the concentration of copper in the bulk water remained below the point which significantly influences the copper release rate (i.e., remain in the region where the reaction mechanism controls the release) but still large enough to be accurately measured.

This use of a continuous-flow system resulted in a relatively high level of precision. Considering that corrosion measurement techniques, such as weight loss, are typically only 20-50% reproducible (Fontana, 1986), concentration measurements under continuous-flow conditions provided a better means for directly quantifying copper dissolution rates. The steady-state trends from the continuous-flow experiments were well-defined and provided an easier means, compared to the initial batch experimental slope, for determining copper concentrations used in calculations of initial copper release rates. These values were subsequently used in the evaluation of the release rate model.

Under reaction-limited conditions (low copper concentrations), the present model predicts that the concentration will decrease in inverse proportion to the flow rate (i.e., $F_{Cu_b}$ is a constant). This trend is clearly shown in Figure 4.7, where doubling the flow rate from 16 to 32 mL min$^{-1}$ decreased the concentration by approximately half (from 133.2 $\mu$g L$^{-1}$ to 73.3 $\mu$g L$^{-1}$). This was not true, however, for the 2 mL min$^{-1}$ flow rate where the copper
concentration only doubled relative to the value at 8 mL\(\cdot\)min\(^{-1}\). This was attributed to a reduction in dissolution because the flow rate was too low to prevent an appreciable build-up of copper in the bulk water to a supersaturated condition resulting in precipitation losses from the solution (as occurred under batch conditions).

The peak in copper concentration under continuous-flow conditions (Figure 4.7) was likely due, initially, to the rapid dissolution of the copper-rich film present on the copper plates after the 48 hour conditioning period prior to the experiment, similar to observations under batch conditions. When this conditioned surface was placed into lake water which has a low copper concentration, the copper-rich film dissolved rapidly in this new solution as illustrated in Figure 4.3. Once the film dissolved into the solution, the results suggest that copper began to rapidly oxidize in the water resulting in a rapid increase in copper concentration in solution which is consistent with results found by Kruger (1961). Under continuous-flow conditions at high flow rates, the rapidly increasing copper concentration in the bulk solution was quickly reduced; however, the flow rate of 2 mL\(\cdot\)min\(^{-1}\) was not high enough to prevent the copper concentration from approaching the saturation level, and so precipitation and passivation events suppressed the copper release rate.

The time taken for the continuous-flow experimental concentration curves to reach steady-state were examined to determine whether the phenomena observed in the vessel was the result of concentration effects. At all of the flow rates examined, the copper release curves followed similar trends. There was a rapid increase in copper concentration followed by a decrease to a steady release rate; the higher flow rates achieving this steady rate at shorter times than the lower flows. A comparison of the number of residence times required
to achieve a steady release rate showed that for all of the flow rates, more than three residence times were required to reach a steady release rate indicating that the decrease to steady-state could not be explained only by flushing copper from the vessel and that other phenomena were occurring in the system. These results suggest that surface changes influenced the changing copper release rate.

The number of residence times required to reach steady-state at the low flow rate (2 mL\textpermin) was lower than expected compared to the number of residence times required at higher flow rates. This may be explained by observing that the copper concentration at the low flow approaches a saturated copper concentration which results in the precipitation of copper species from solution. Therefore, copper is taken from solution by two mechanisms under low flows: flushing with fresh lake water and precipitation. This result agrees with the batch experimental results; namely, that a build-up of copper in solution decreases the copper release rate and does not result in an accurate estimate of copper release. The low flow rate of 2 mL min\textsuperscript{-1} does not provide an accurate estimate of release rate because there is a build-up of copper within solution which results in precipitation of copper from solution which underestimates the copper release rate.

Work done by Kruger (1961) describes the events that occur when copper is placed into water. Initially there is a rapid dissolution of copper into solution while Cu\textsubscript{2}O forms. This explains the initial peak in copper concentration under continuous flow conditions when copper is placed into solution. This peak is more evident in low flow experiments whereas at 32 mL\textpermin only a slight increase is observed since the higher flow rates flush the copper from solution faster and the reaction products are moved away from the surface faster.
allowing the surface to oxidize at a faster rate. Following this initial peak in copper concentration, there is a typical decrease in copper release rate with increasing time. This reduction is due to the flow removing copper from solution while at the same time the copper surface continues to change and oxidize which also reduces copper release. Kruger (1961) found that the Cu₂O film on the copper surface formed rapidly reaching a limiting thickness that remained constant for a few hours. Once the limiting thickness was achieved, CuO began to form. This results in two competing reactions, i.e., for CuO and Cu₂O. These competing reactions, reduce the copper release into the solution resulting in a reduction in copper release rate which ends in a plateau or steady-state release rate. Kruger noted that, within six hours, a film of 1000 Å was observed on the copper surface, indicating a rapidly forming surface layer.

4.5.4 Continuous-Flow Model Parameters

The results from the continuous-flow experiments at their steady-state points were substituted into the release-rate model for continuous-flow reaction-limited conditions, Equation (4.19). As shown in Figure 4.12, the release rates were approximately constant at flow rates greater than 8 mL·min⁻¹ (average value of 25.8 ± 3.5 mg·m⁻²·day⁻¹) indicating that these values are within the reaction-limited regime of the proposed model. At a flow rate of 2 mL·min⁻¹, the release rate was substantially lower, approximately 10 mg·m⁻²·day⁻¹.

The assumption that the steady-state region of the continuous-flow experiment corresponded to the reaction-limited regime was verified by changing the mass transfer coefficient under stirred conditions (Figures 4.8 and 4.9). At lower stirrer speeds (< 45 rpm; Figure 4.8) there was no detectable difference between the copper release rate in the stirred
and agitated vessels while at very high stirrer speeds of 300 and 500 rpm (Figure 4.9), there was a very slight increase (approximately 17 %) in copper release rate, but the rate returned to the steady-state values when the experiment was resumed on the shaker table.

In order to further test the conclusion that mass transfer effects were insignificant, the mass transfer coefficients for the stirred continuous-flow experiments were estimated by substituting the water velocity measurements into the mass transfer correlation for laminar flow between parallel plates (Pickett and Ong, 1974),

\[ k_m = 0.332 \frac{D}{x} Re_x^{\frac{1}{2}} Sc^{\frac{1}{2}} \left[ \frac{1}{H/x} \right]^{\frac{1}{2}} \]  

(4.10)

where \( k_m \) is the local mass transfer coefficient (units of m s\(^{-1}\)), \( D \) is the diffusion coefficient (units of m\(^2\) s\(^{-1}\)), \( Re_x \) is the Reynolds number, \( Sc \) is the Schmidt number, \( H \) is the hydrodynamic entrance length (units of m) and \( x \) is the distance in the flow direction from the hydrodynamic leading edge. Equation (4.10), shows that the mass transfer coefficient, \( k_m \), varies with the square root of velocity. If the release rate process was mass transfer controlled, an increase in the velocity within the vessel by a factor of ten would increase the mass transfer coefficient and rate by more than a factor of three (i.e., \( \sqrt{10} \)). Since the release rate increased by only 17 % under stirred conditions at 300 and 500 rpm, the copper release rate was largely reaction limited. Furthermore, if Equation (4.22) is used to estimate the mass transfer coefficient, \( k_m \), a copper release rate of 7,000 mg m\(^{-2}\) day\(^{-1}\) is obtained, which is much higher than the experimentally determined release rate of 25.8 mg m\(^{-2}\) day\(^{-1}\). This supports the hypothesis that the processes involved in the present continuous-flow copper
release rate experiments were reaction rate limited, and were not influenced significantly by mass transfer.

A comparison of copper release rates measured under batch and continuous-flow conditions is shown in Table 4.2. The values are comparable, but the batch release rates depend on the point chosen to calculate the initial slope of the batch experimental results. The copper concentration measured under continuous-flow conditions provided a more objective means of obtaining copper release rates. In addition, the continuous-flow experiments provided more repeatable results whereas the batch experimental results (first exposure periods, Table 4.2) differed by approximately 17%. Nevertheless, if care is taken to obtain the initial slope data (i.e., at concentrations far below the supersaturated copper concentration) then batch experiments can be useful for quickly estimating copper release rates.
Figure 4.12: Copper release rate, $k_r$, as a function of flow rate based on the continuous-flow model. Error bars are the standard errors of the calculated average release rates (Note: the error bars are smaller than the symbol size).
Chapter 4: Measurements and Modeling of Copper Release Rates in Lake Water

Other experiments have been conducted to determine copper release rates under batch conditions. The study by Brock and Popplewell (1979) found that copper release rates into fresh water were 50 mg·m⁻²·day⁻¹, whereas copper release rates into Florida tap water were approximately 75 mg·m⁻²·day⁻¹ (Akkaya and Ambrose, 1987). These values differ from the results obtained in the present study likely because the water chemistries were unlike those in Lake Ontario water (i.e., higher pH and chloride levels). Bailey and Wright (1971) have also suggested that a linear model could be used to describe the release of copper into water under the simplest of experimental conditions in which there is no water flow and the corrosion rate is constant, such as under the initial phase of the batch experiments. This is consistent with results obtained under batch condition experiments performed in this thesis.

The results from the continuous-flow experiments are consistent with those of Feng et al. (1996) which showed that the corrosion rate of copper was limited by the diffusion of copper ions through the copper oxide, a process which was included in the reaction mechanism of the present model. Stone et al. (1987) also found that the corrosion rates of copper in tap water were dependent upon the movement of reactants through the oxide film and the rate of reaction at the copper surface. Hilburn (1983) found that mass transfer effects were rate limiting at a water pH of 6.3 (standing river water), which is lower than Lake Ontario water and likely to produce greater reaction rates, thereby causing mass transfer processes to become more significant. Hilburn concluded that, as the pH increased, the control by chemical kinetics and diffusion through the oxide became comparable, but mass transfer through the solution was still rate-limiting. This may result from the different chemistries of the water used in the Hilburn study and the lake water used in the present
study (e.g., conductivity and oxygen concentration) or the different flow conditions. These studies were conducted using electrochemical techniques and weight loss measurements which do not directly quantify copper dissolution rates (the goal of this work), however the rate controlling mechanisms of the first two studies are consistent with the present model.

As stated initially, copper plates prevent zebra mussel attachment (Dormon et al., 1996) hence, the results from this Chapter suggest that an average copper release rate of 26 mg·m⁻²·day⁻¹ is sufficient to prevent zebra mussel biofouling. There are several other copper-containing materials which also prevent zebra mussel attachment such as copper-nickel alloys (Dormon et al., 1996) and in the following Chapters, copper release rates from these materials will be quantified for comparison with copper plates to determine the minimum initial copper release rate required to prevent biofouling and to gain a better understanding of the way in which copper prevents zebra mussel attachment.

4.6 Conclusions

Copper release rates in lake water under batch conditions were influenced by a progressive increase in copper concentration to a supersaturated region, which resulted in the precipitation of copper species from solution and the passivation of the copper surface. This indicated that the batch experiments may not provide an accurate assessment of the copper release rate into natural lake water conditions which have low copper concentrations. However, the application of the batch experimental approach should not be overlooked. The initial slope of the batch experimental results provided a comparable measure of the copper release rate to that obtained from the continuous-flow experiments and can be used for quickly estimating copper release rates. The batch experiments are also useful for rapidly
estimating release rates and for determining saturated concentrations and the behaviour of solutions under stagnant conditions in situations such as water piping or heat exchangers.

The continuous-flow experimental method, using flow rates greater than 2 mL•min⁻¹, provided an accurate means for evaluating copper release rates into lake water. These copper release rates can be modeled by considering two processes: the "reaction mechanism" which includes both the kinetics of copper corrosion and the diffusion of copper ions through the oxide layer, and the mass-transfer mechanism by which the reaction products move away from the copper solid-water interface. The steady-state release rate at low copper concentrations (< 0.25 mg•L⁻¹) is reaction limited with a value of 26 mg•m⁻²•day⁻¹. Converting this copper release rate into a corrosion rate results in a value of 1.1 µm•yr⁻¹. This value is much lower than corrosion rates found in seawater (87 µm•yr⁻¹, Ijsseling et al., 1982) and tap water systems (5.8 µm•yr⁻¹, Hilburn, 1983). These results indicate that the use of copper in a biofouling prevention application would probably result in a loading much less than the current loading which results from tap water systems.

Under batch experimental conditions, the copper concentration in the bulk water reached a supersaturated state. Upon reaching supersaturation, the copper concentration remained steady at a meta-stable plateau while copper complexes precipitated from the solution. Once the complexation of copper had been initiated, the copper concentration in solution then decreased due to the formation of copper precipitates which fall to the bottom of the test vessel or onto the copper surface impeding corrosion.

Copper release rates obtained through these experiments can be used to help explain the zebra mussel antifouling properties of various copper materials in freshwater
environments and aid in the design of copper-containing materials for anti-fouling applications. The data can also guide studies investigating the effect of copper usage on freshwater ecosystems. However, the work in this thesis does not allow for the quantification of a concentration threshold since the flow conditions, and therefore the thicknesses of the concentration boundary layers, over the plates were extremely variable. Nevertheless, from an engineering standpoint, the work in this thesis in conjunction with previous zebra mussel recruitment studies (Dormon et al., 1996) has revealed a useful correlation between zebra mussel biofouling resistance in typical lake conditions and a material’s copper dissolution rate under well-mixed flow conditions into bulk water that is essentially free of copper.
Chapter 5
Copper and Nickel Dissolution Rates from Copper-Nickel Alloys in Fresh Water

5.1 Introduction

Recent recruitment studies have been done to compare the zebra mussel anti-fouling characteristics of some common construction materials. It was found that zebra mussels do not attach to copper and certain copper-nickel alloys (Dormon et al., 1996; Kilgour and Mackie, 1992).

In order to quantify the potential loading of copper to the environment that would be realized with copper use, initial copper release rates from copper plates were measured in Lake Ontario water, as discussed in Chapter 4. It was found that a copper release rate of 26 mg·m⁻²·day⁻¹ would be initially realized when using copper to prevent zebra mussel biofouling. Since alloys of lower copper content, such as Cu:Ni 90:10, Cu:Ni 80:20, and Cu:Ni 70:30, have also been shown to prevent zebra mussel biofouling (Dormon et al., 1996) it was of interest to obtain initial copper release rates from the copper-nickel alloys and so determine the corresponding minimum rate of release for the desired biofouling resistance and gain a better understanding of the anti-fouling mechanisms of copper-containing materials. A second objective was to obtain copper and nickel release rates to help address potential environmental impacts and regulatory issues pertaining to potable water.

Several studies have been conducted to test the corrosion rates of copper-nickel alloys, as mentioned in Chapter 2 (Al-Hajji and Reda, 1995; 1993; Beccaria and Crousier, 1991; Kato et al., 1980a; b; Efird, 1976; LaQue and Clapp, 1945) but these experiments were performed in
sea water or NaCl solutions. The behaviour of copper-nickel alloys in fresh water environments could not be inferred from these experiments because copper-nickel alloys behave differently in sea water than in fresh water (Hummer, 1968).

5.1.1 Copper Release Rate Model

In Chapter 4, a model was developed to describe the rate of dissolution of copper in fresh water. Copper dissolution was viewed as the result of four processes: (i) a "reaction mechanism" which combines both the copper corrosion kinetics and the diffusion of copper ions through the developing oxide layer; (ii) a precipitation reaction which takes soluble copper species out of solution; (iii) a "mass transfer mechanism" in which reaction products move away from the copper solid-water interface into the bulk lake water; and (iv) a passivation mechanism in which a copper-rich layer forms on the copper surface, decreasing the corrosion rate. A copper release rate model was derived for both batch and continuous-flow experimental conditions under reaction-limited conditions.

The model for the batch copper release rate under reaction-limited conditions is given in Equation (4.10). The copper release rate model under continuous-flow conditions for the reaction-limited region is Equation (4.17).

In this Chapter, the release rates of copper and nickel from three copper-nickel alloys (Cu: Ni 90:10, Cu: Ni 80:20, and Cu: Ni 70:30) in fresh water are quantified. These results are used to determine whether the model, developed for the dissolution of copper in fresh water (Chapter 4), can be used to describe the initial release rate of copper from copper-nickel alloys. In addition, linear polarization measurements, used to characterize the copper-
containing materials, are described and compared with the release rate results. The results from this Chapter are used to answer Objectives 4 and 5 of this thesis, namely:

- To quantify the release of copper and nickel from copper and copper-nickel alloys in fresh water; and
- To develop a model to predict the rate of copper release from copper and copper-nickel alloys into fresh water.

5.2 Methods and Materials

5.2.1 Copper and Nickel Release Rate Experiments

Copper and nickel release rate experiments were performed using copper-nickel alloys under both batch and continuous-flow conditions as described in Chapter 4 so that the results from these experiments could be directly compared to the results from the tests using copper plates. These methods are briefly summarized below.

5.2.1.1 Batch Experiments

The experiments were conducted in the low-density polyethylene (LDPE) lined plexiglass vessel (16 cm x 5 cm x 25 cm) (Figure 4.1) as used in the copper release rate studies described in Chapter 4. The vessel was held on a shaker table and gently agitated in order to have well-mixed conditions in the vessel. Four slotted polytetrafluoroethylene (PTFE) bars were used to hold the copper-nickel alloy plates upright in the vessel, and each vessel held four copper-nickel alloy plates having dimensions of 8 cm x 15.5 cm x 0.16 cm. An air pump connected to LDPE tubing was used to maintain saturated oxygen conditions within the vessel. The vessel was covered with aluminum foil to avoid changing light
conditions which can affect oxide layer formation (Kruger, 1959), and was closed in order to prevent water loss through evaporation. The water quality was the same as under the experiments conducted in Chapter 4 (see Table 4.2).

Prior to testing, plates of Cu: Ni 90:10, 80:20, and 70:30 (compositions are shown in Table 5.1, see phase diagram given in Figure 5.1) were etched using a sulphuric-nitric acid dip (1 part sulphuric acid : 1 part nitric acid : 1 part water; Snogren, 1974) in order to achieve a uniform, initial surface condition. Four plates of the same copper-nickel alloy were placed into the PTFE holders and one litre of filtered (0.2 mm nominal) Lake Ontario water was added to the vessel. Temperature and pH were monitored throughout the duration of the experiments (temperature = 21 ± 0.5 °C, pH = 8.2 ± 0.1). Water samples were taken from the middle of the vessel at regular intervals, acidified to a pH < 2 using environmental grade nitric acid, and analyzed for copper and nickel concentration using graphite furnace atomic absorption spectrometry (GFAAS) (EPA, 1990) which has a detection limit of 0.4 μg·L⁻¹ for copper and 0.2 μg·L⁻¹ for nickel.
Table 5.1: Compositions of the copper-nickel alloys used in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>Cu (%)</th>
<th>Ni (%)</th>
<th>Fe (%)</th>
<th>Cu:Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu:Ni 90:10</td>
<td>88.7</td>
<td>10.3</td>
<td>1.0</td>
<td>8.6 : 1</td>
</tr>
<tr>
<td>(C706)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu:Ni 80:20</td>
<td>79</td>
<td>21</td>
<td>-</td>
<td>3.8 : 1</td>
</tr>
<tr>
<td>(C710)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu:Ni 70:30</td>
<td>70</td>
<td>30</td>
<td>-</td>
<td>2.3 : 1</td>
</tr>
<tr>
<td>(C715)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.2.1.2 Double-Exposure Experiment

A second batch experiment, a "double exposure" experiment similar to that conducted in Chapter 4, was repeated using the Cu:Ni 80:20 alloy. Freshly etched Cu:Ni 80:20 plates were placed into the batch experimental set-up for one month. At the end of the batch experiment, the plates were removed from the vessel, rinsed with filtered lake water and added to one litre of fresh, filtered Lake Ontario water in another vessel. Bulk water samples were taken at regular time intervals, acidified to a pH < 2 using environmental grade nitric acid, and analyzed for copper and nickel content using GFAAS.

5.2.1.3 Continuous-Flow Experiments

The batch experimental set-up, described above, was modified to include an inflow and outflow port (Figure 4.1). A continuous flow of filtered Lake Ontario water was supplied by a peristaltic pump and water flow rates were determined by measuring the time to fill a volumetric flask. Again, the vessel was agitated on a shaker table throughout the entire experiment.
Initially, four acid-etched copper-nickel plates of the same composition, were conditioned in aerated, filtered Lake Ontario water under dark conditions for 96 hours and then were placed into one litre of fresh, filtered Lake Ontario water in the continuous flow set-up. Flow rates of 10 and 16 mL·min⁻¹ were selected for the continuous flow experiments based on the results obtained in Chapter 4. The results from the copper release rate experiments in Chapter 4 had indicated that these flow rates were sufficient to prevent the copper concentration within the bulk solution from approaching the value which would influence the copper release rate. Water samples were taken from the bulk solution at the outlet port of the vessel at regular time intervals, acidified to pH < 2 using environmental grade nitric acid, and analyzed for copper and nickel content using GFAAS.

5.2.2 Linear Polarization Measurements

A conventional three electrode test cell was used for the polarization resistance measurements. The test cell consisted of two graphite counter electrodes and a saturated calomel electrode (SCE) as the reference electrode which was isolated in a separate vessel and connected to the corrosion cell using a luggin capillary filled with the electrolyte solution. All measurements are reported with respect to the SCE. A 3.4 % sodium chloride solution was used in order to replicate the results of North and Pryor (1970). Anodic polarization studies were conducted using a Princeton Applied Research EG&G Potentiostat/Galvanostat (Model 273).

The surface surrounding a 1 cm² area of freshly etched copper and copper-nickel alloy (Cu:Ni 70:30, 80:20, and 90:10) plates was masked using Amercoat 90 Epoxy (Ameron
Incorporated, Monterey Park, California) prior to testing. Some of the plates were tested following the application of epoxy while others were placed into covered tanks containing aerated, filtered Lake Ontario water and removed at various times for testing in order to monitor the rate of oxide layer growth over time for comparison with the results from the release rate studies.
5.3 Results

5.3.1 Copper and Nickel Release Rate Experiments

5.3.1.1 Batch Experiments

The results from the batch experiments are shown in Figures 5.2a and 5.2b for copper and nickel concentrations, respectively. The results from the copper batch experiments (Chapter 4) are included in Figure 5.2a for comparison. The initial slope of the copper concentration versus time curve (up to the 24 hour point) varied for the three copper-nickel alloys, with a ranking of Cu:Ni 90:10 > Cu:Ni 80:20 > Cu:Ni 70:30. The initial slope of the concentration versus time curve for the copper plates was similar to the slope for Cu:Ni 90:10. Overall, the change in copper concentration with time for the copper-containing alloys was similar; the copper concentration in the vessels increased rapidly to a peak value and then decreased slowly to between 0.7 mg\(\text{L}^{-1}\) and 0.4 mg\(\text{L}^{-1}\) over approximately 700 hours.

The change in nickel concentration with time was essentially the same for Cu:Ni 80:20 and Cu:Ni 70:30, reaching values between 6.5 mg\(\text{L}^{-1}\) and 8 mg\(\text{L}^{-1}\), respectively, after 800 hours. The results for Cu:Ni 90:10 were significantly lower, reaching a nickel concentration of approximately 2.5 mg\(\text{L}^{-1}\). In contrast to the copper concentrations, the nickel concentrations steadily increased throughout the experiment.

In order to investigate whether the copper trends observed in the batch experimental results were due to the increase in copper concentration within the bulk lake water, as predicted by the model for copper developed in Chapter 4, a double exposure experiment was
performed using the Cu:Ni 80:20 alloy. Figure 5.3 shows that the two copper concentration curves are very similar, confirming that the release rate under batch conditions is influenced by the build-up of copper concentration within the bulk liquid rather than passivation from a growing oxide layer. This result agrees with that found in Chapter 4 for copper plates.
Figure 5.1: Phase Diagram for Copper-Nickel Alloys.
Figure 5.2a: Comparison of results from the batch experiments using copper-nickel alloys showing the change in concentration of copper with time.
Figure 5.2b: Comparison of results from the batch experiments showing the change in concentration of nickel with time.
5.3.1.2 Continuous-Flow Experiments

The copper concentrations in the bulk liquid samples from the continuous-flow experiments were converted into copper release rates using Equation (4.8), and the results are shown in Figures 5.4a, b, and c; the values are summarized and compared to the copper release rate from Chapter 4 in Table 5.2. The copper release rates reached steady-state conditions at different times; Cu: Ni 90:10 and 70:30 after approximately 50 hours, and 80:20 after 250 hours. The copper release rates from Cu: Ni 90:10 fluctuated more than those for the other alloys. In all cases, the concentrations were inversely proportional to the flow rate, resulting in similar steady-state release rates for the particular alloy. The steady-state copper release rate decreased with decreasing copper content, with Cu: Ni 90:10 having a value of approximately 28 mg m\(^{-2}\)day\(^{-1}\), followed by 80:20 and 70:30, 6 mg m\(^{-2}\)day\(^{-1}\) and 2 mg m\(^{-2}\)day\(^{-1}\), respectively.

The effect of conditioning time prior to testing was investigated using the Cu: Ni 70:30 alloy at a flow rate of 16 mL\(\cdot\)min\(^{-1}\) (Figure 5.5). Conditioning periods of 96 hours and 1 month resulted in indistinguishable steady-state copper release rates. Initially however, there was a larger copper release rate from the Cu: Ni 70:30 alloy plates which had been conditioned for a longer time period due probably to the loosely adherent copper layer dissolving rapidly into solution.

The nickel concentration results from the continuous-flow experiments were also converted into release rates using Equation (4.19), and the results are shown in Figures 5.6a,
Figure 5.3: Copper release curves from the double exposure experiments comparing the two exposure periods of Cu:Ni 80:20 under batch conditions.
Figure 5.4a: Comparison of the change in copper release rate with flow rate for the copper-nickel alloys Cu:Ni 90:10. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.4b: Comparison of the change in copper release rate with flow rate for the copper-nickel alloys Cu:Ni 80:20. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.4c: Comparison of the change in copper release rate with flow rate for the copper-nickel alloys Cu:Ni 70:30. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.5: Effect of conditioning time prior to testing, on copper release rate with Cu:Ni 70:30. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
b, and c, and are summarized for comparison in Table 5.2. The steady-state for nickel release was achieved in approximately the same amount of time as for copper and varied for the different alloys; with 90:10, 80:20, and 70:30 reaching steady-state after 400 hours, 260 hours, and 170 hours, respectively. Similar to the copper results, the nickel concentrations were inversely proportional to the flow rate, resulting in the same release rate at steady-state for a particular alloy. As shown in Table 5.2, the nickel steady-state release rates decreased with increasing nickel content with copper-nickel 90:10 having the highest nickel release rate of 5.2 mg m\(^{-2}\) day\(^{-1}\), followed by 1.5 mg m\(^{-2}\) day\(^{-1}\), and 0.8 mg m\(^{-2}\) day\(^{-1}\) for Cu:Ni 80:20 and Cu:Ni 70:30, respectively.

The release rate data obtained for both copper and nickel under continuous-flow conditions were not as repeatable as the data obtained for pure copper. This is shown in Figures 5.4c and 5.6c for Cu:Ni 70:30 in which replicate experiments were conducted at 16 mL min\(^{-1}\). In the first experiment the steady-state copper release rate was 1.7 mg m\(^{-2}\) day\(^{-1}\) and the second had a value of 2.3 mg m\(^{-2}\) day\(^{-1}\) (a difference of approximately 35 %). The steady-state nickel release rate obtained in the first experiment was 0.76 mg m\(^{-2}\) day\(^{-1}\), and the replicate release rate value was also about 35 % higher, at 0.98 mg m\(^{-2}\) day\(^{-1}\).

5.3.2 Linear Polarization Measurements

The results from the linear polarization studies using freshly etched copper-nickel alloys are shown in Figure 5.7. As the copper content of the alloy increased, the linear polarization resistance decreased indicating an increase in the corrosion rate (slopes of curves in Figure 5.7). This trend was consistent with the results from the copper release rate studies.
in which the greatest release rates were obtained for copper, followed by Cu: Ni 90:10, Cu: Ni 80:20, and Cu: Ni 70:30.

The linear polarization measurements were then used to characterize the surfaces of the copper-nickel alloys as a function of exposure time to lake water (Figure 5.8). Copper was not included in the data set because it was not possible to obtain repeatable results for the copper plates due to the large corrosion rate or low slope. In the initial three days of exposure to lake water after acid etching the copper-nickel alloy plates, the linear polarization resistance increased rapidly reaching a steady-state condition after approximately three days.
Figure 5.6a: Comparison of the change in nickel release rate with flow rate for the copper-nickel alloys Cu:Ni 90:10. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.6b: Comparison of the change in nickel release rate with flow rate for the copper-nickel alloys Cu:Ni 80:20. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.6c: Comparison of the change in nickel release rate with flow rate for the copper-nickel alloys Cu:Ni 70:30. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample).
Figure 5.7: Results from the linear polarization studies using freshly etched copper-nickel alloys.
5.4 Discussion

Under batch conditions, the change in copper concentration with time for the copper-nickel alloys followed a trend similar to that obtained for copper plates (Figure 5.2a) which was characterized by a rapid increase in copper concentration followed by a plateau region and then a decrease with increasing time. The plateau and subsequent decrease in copper concentration was explained using results from previous studies reported in literature (Chapter 4) which suggested that before the precipitation of the oxide species can occur, a supersaturated copper concentration close to the copper surface is required. The explanation for the subsequent decrease in copper concentration to a plateau and then to a steady-state concentration was due to precipitation, mass-transfer limitations and copper-layer formation.

These findings were used to interpret the results from the batch experiments, using copper-nickel alloys, and it is hypothesized that the copper release rate in the bulk solution is suppressed by the approach to a supersaturated copper concentration. This explanation is supported by the "double-exposure" experiment using Cu:Ni 80:20 (Figure 5.3) which showed that the copper release rate was influenced by the progressive build-up of copper concentration to a supersaturated state within the bulk liquid and not the passivation of the copper. Therefore, as concluded in Chapter 4, batch conditions do not provide a suitable test condition for measuring copper release rates due to the influence of the increasing copper concentration within the bulk liquid. Continuous-flow experiments should provide a better means for quantifying copper and nickel release rates from copper-nickel alloys.
Figure 5.8: Results from the linear polarization studies using lake-water conditioned copper-nickel alloys.
Under batch conditions, the nickel concentration within the vessel increased with time. This trend was different than the results obtained for copper. This may be explained by comparing the solubility of copper and nickel species. The interpretation of the copper batch data suggests that the increasing copper concentration past solubility limits within the vessel results in the precipitation and passivation of the surface which results in a decreasing copper release rate. In Chapter 2 the solubilities of copper and nickel are compared. The nickel solubility limit is greater than the values for copper which indicates that more nickel can dissolve into water before precipitating from solution, hence the nickel concentration curve continues to rise with time. This result is consistent with the copper batch data, namely, the release rate is dependent upon the concentration of the species within solution. In addition, the copper to nickel release rates are proportional to the Cu:Ni composition ratio of the alloy and the increase in nickel concentration over time also suggests that copper continues to come off with the nickel and precipitate over the duration of the experiment. The presence of copper oxides on the copper-nickel alloys is confirmed in Chapter 6 using X-ray Photoelectron Spectroscopy (XPS) investigations on conditioned plates.

The continuous-flow experiments (Figures 5.4a,b,c and 5.6a,b,c) provided a means to measure the release rate of copper from copper-nickel alloys into fresh water without the influence of increasing copper concentrations. The method did not provide as high a level of precision in quantifying both the copper and nickel release rates as was obtained for the copper plates (Chapter 4). The maximum difference of 35 % between replicate experiments is, however, an acceptable error in corrosion measurements (Fontana, 1986). The results
from the continuous-flow experiments were used to test the ability of the model to describe
the release of copper from copper-nickel alloys.

These results support the application of the release rate model developed for copper
plates to the copper-nickel alloys. For the copper-nickel alloys, specifically Cu:Ni 80:20
(Figures 5.4b and 5.6b) and 70:30 (Figures 5.4c and 5.6c), both the copper and nickel release
rates reached the same steady-state values at different flow rates, F, in relatively short times
(i.e., FCu was constant with varying F) which is consistent with the copper release rate
model for the reaction-limited regime. Copper and nickel release rates from Cu:Ni 90:10
reached steady-state values in a shorter time than observed for the other alloys and fluctuated
around the steady-state value, but the release rate did not change greatly with flow rate
indicating that the results from Cu:Ni 90:10 were also within the reaction-limited regime.

It is interesting to note that the initial copper release rate from the Cu:Ni 70:30 plates,
which were conditioned for one month, was greater than the release rate from the Cu:Ni
70:30 plates which were conditioned for only 96 hours before the continuous-flow
experiments (Figure 5.5). This observation is consistent with the continuous-flow release
rate results for copper. As explained in Chapter 4, when the copper or copper-nickel plates
were pre-conditioned under batch exposure, the build-up of copper concentration in the bulk
solution allowed a copper-rich film to form on the surface of the copper alloy plates. Upon
exposure to the low copper concentration of the fresh lake water under continuous-flow
conditions, the copper-rich layer on the conditioned copper plates was rapidly released into
solution, as observed in the double-exposure experiments, but the copper concentration did
not build up due to the continuous flushing of the vessel with fresh lake water. This result indicates that the copper-rich film present on the copper and copper-nickel plates is easily removed and allows the alloys, which have been pre-conditioned for various times, to corrode and reach similar steady-state corrosion rates; an observation similar to the results from the double-exposure experiments.

The results from the continuous-flow experiments shown in Table 5.2 indicate that as the copper composition within the alloy increased the copper release rate also increased, whereas the increasing nickel content in the alloy resulted in a decreasing nickel release rate. These results show that the increasing nickel content decreases the dissolution rate of copper into fresh water or the amount of copper available for release. This behaviour may be explained based on the results of previous studies into other aqueous solutions by other investigators. North and Pryor (1970) determined a corrosion mechanism for copper-nickel alloys in 3.4 \% NaCl solution. They found that as the nickel content of the alloy increased, a larger number of Ni\(^{2+}\) ions replaced the Cu\(^{+}\) in the oxide film (Cu\(_2\)O) resulting in an increase in the electron and ion resistances of the copper oxide reaction products on the copper-nickel alloys. This increase in resistance results in improved protection of the oxide and a reduction in corrosion rate (North and Pryor, 1970). Another study by Castle (1979) which examined high temperature oxidation of copper-nickel alloys showed that increasing nickel compositions in copper-nickel alloys resulted in a decrease in the porosity of the oxide layers.

A review by Pickering et al. (1986) of studies which examined copper-nickel alloy
Table 5.2: Comparison of copper and nickel release rates from continuous-flow experiments.

corrosion in NaCl solutions indicated that the reduction in corrosion rate is due to the poor catalytic oxygen reduction reaction characteristics of the corrosion layer formed on the alloys. Therefore, as the nickel content increases from 10% to 30%, a more protective oxide layer consisting of increasing amounts of nickel forms on the alloy, inhibiting the cathodic reaction and decreasing the release of copper and nickel into fresh water.

Another trend observed in the data in Table 5.2 is the corresponding ratios of copper to nickel dissolution rates and of copper to nickel compositions in the alloys. The copper and nickel release rates from Cu:Ni 80:20 and Cu:Ni 70:30 occur in the same ratios as found in the alloy composition. However, the results from Cu:Ni 90:10 did not occur in the same ratio as the alloy; more nickel was released with respect to the copper from the alloy. This may have resulted from the presence of a thicker oxide layer which has been noted to form on the
Cu:Ni 90:10 alloy (North and Pryor, 1970) compared to the Cu:Ni 70:30 alloy. It may also be due to the error in estimating the average dissolution rate from the copper-nickel alloy due to the fluctuations around the steady-state point since the release rates from the Cu:Ni 80:20 and 70:30 had relatively constant steady-state values (see Table 5.3).

Another observation from the continuous-flow experiments was the number of residence times required to reach steady-state conditions. For Cu:Ni 90:10, experiments conducted at 10 and 16 mL·min⁻¹ required 176 and 150 residence times, respectively, for the copper release rate to reach steady-state and 176 and 125 residence times, respectively, for the nickel release rate to reach steady-state. For Cu:Ni 80:20, experiments conducted at 10 mL·min⁻¹ and 16 mL·min⁻¹ required 280 and 188 residence times, respectively, for the copper release rate to reach steady-state and 290 and 182 residence times, respectively, for the nickel release rate to reach steady-state. Finally Cu:Ni 70:30, experiments conducted at 10 and 16 mL·min⁻¹ required 170 and 200 residence times, respectively, for the copper release rate to reach steady-state and 160 and 153 residence times, respectively, for the nickel release rate to reach steady-state. These results agree with the observation that copper and nickel are released at a rate that is proportional to the composition of the alloy. In addition, this result indicates that the changing release rates are due to surface changes with time and not simply the flushing of copper or nickel from the vessel.

A similar trend in release rate was observed for the copper plates (Chapter 4). At higher flow rates, the soluble concentrations within the vessels did not attain high levels and approached their respective steady-states faster. This suggests that the initial release is
handled by the higher flow rates which also prevents concentration build up at the plate surface allowing the surface to corrode without interference from a build-up of soluble species at the solid-water interface. In addition, the high initial concentration at lower flows has to be flushed out which requires longer times at lower flows. However, as time increases and the alloy surfaces change the final release rates represent similar surface conditions resulting in common release rates. This indicates that release rate is a surface effect under continuous-flow conditions.

Table 5.3: Copper Release Rate Data

<table>
<thead>
<tr>
<th>Material</th>
<th>Flow Rate (mL/min)</th>
<th>Number of Data Points</th>
<th>Mean Release Rate (mg/m²/day) ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>8</td>
<td>4</td>
<td>28.4 ± 0.914</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>4</td>
<td>24.8 ± 2.77</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>4</td>
<td>31.3 ± 1.37</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>4</td>
<td>25.7 ± 1.26</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>4</td>
<td>23.3 ± 1.04</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>4</td>
<td>22.6 ± 0.564</td>
</tr>
<tr>
<td>Cu:Ni 90:10</td>
<td>10</td>
<td>11</td>
<td>25.9 ± 3.01</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>19</td>
<td>29.1 ± 3.57</td>
</tr>
<tr>
<td>Cu:Ni 80:10</td>
<td>10</td>
<td>6</td>
<td>5.62 ± 0.354</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>6</td>
<td>4.95 ± 0.754</td>
</tr>
<tr>
<td>Cu:Ni 70:30</td>
<td>10</td>
<td>9</td>
<td>1.61 ± 0.327</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5</td>
<td>1.66 ± 0.436</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>5</td>
<td>2.34 ± 0.366</td>
</tr>
</tbody>
</table>
Other studies have considered the dissolution of copper and nickel from copper-nickel alloys. For example, Beccaria and Crousier (1991) measured the change in copper and nickel concentrations in sea water from Cu: Ni 70:30 alloys, containing various amounts of iron additions, under batch conditions. A similar trend in the change copper and nickel concentrations in the solution to that obtained in this study was found, namely that the ratio of copper to nickel released to solution was similar to the ratios of the metals in the alloys; this was only true for Cu: Ni 70:30 alloys which contained iron additions. Efird (1976) investigated the corrosion rates of copper-nickel 90:10 and 70:30 and found that the corrosion rates and rate of total metal ion release from these copper-nickel alloys after a five year sea water exposure period were one third of the value estimated for copper (62 mg·m⁻²·day⁻¹ compared to 186 mg·m⁻²·day⁻¹). These values were based upon a total weight loss corrosion rate which included both the oxide and dissolution products for copper and nickel. In addition, the values were the result of only one measurement on a single test plate after a five year exposure period, which cannot carry a high level of confidence. LaQue and Clapp (1945) investigated the corrosion rates of copper and copper-nickel alloys in natural sea water by performing a single weight loss measurement on materials which had been exposed to biofouling conditions. They found that after five days of sea water exposure, copper had the lowest weight loss (i.e., corrosion rate) compared to Cu: Ni 80:20 and Cu: Ni 70:30 but at longer exposure periods, the copper alloy had the greatest corrosion rate followed by Cu: Ni 80:20 and then Cu: Ni 70:30. The values of corrosion rate over the final
eleven days of a sixteen day exposure were: pure copper - 4200 mg m\(^{-2}\) day\(^{-1}\), Cu:NI 80:20 - 3900 mg m\(^{-2}\) day\(^{-1}\), and Cu:NI 70:30 - 2500 mg m\(^{-2}\) day\(^{-1}\). In the two latter studies, although the ranking of corrosion rates was similar to the results from the present studies, the corrosion values were significantly higher, likely because the testing was performed in sea water, and fouling organisms were present on the surface which could affect the corrosion rate and passivation of the surface (Claudi and Evans, 1992). In addition, these results cannot be directly compared to the results of the present studies because they were obtained from weight loss measurements which include losses to both the oxide and solution thereby overestimating the dissolution rate of copper.

In order to evaluate the linear polarization experimental method, the results from the present studies were compared to those of North and Pryor (1970). A comparison of the slopes (i.e., the polarization resistance) of the results obtained in this study (Figure 5.7) with the results of North and Pryor (Table 5.4) shows that the result for Cu:NI 70:30 was similar to the value obtained by North and Pryor, with a difference of 33 % (which is an acceptable error in corrosion measurements (Fontana, 1986)). The values obtained for Cu:NI 90:10 were less than those obtained by North and Pryor, perhaps due to differences in sample preparation and experimental technique (i.e., use of the luggin capillary) but the relative ranking from the two studies was similar. Figure 5.7 shows that the linear polarization curve for Cu:NI 70:30 had the largest slope and therefore the lowest corrosion rate, whereas Cu:NI 90:10 had the lowest slope or the greatest corrosion rate. These results can be directly compared to the
Table 5.4: Comparison of results from linear polarization measurements in the present study with the results from North and Pryor (1970).

release rate data, which shows that both the copper and nickel release rates were largest from Cu:Ni 90:10, followed by Cu:Ni 80:20, and finally Cu:Ni 70:30, consistent with the linear polarization results.

The results from the linear polarization studies (Figure 5.8), using lake water exposed plates, show that the corrosion rate is rapid within the first three days, for all of the copper-nickel alloys, and then remained constant for a time period of at least 30 days. These results correspond to the copper release rate results obtained for Cu:Ni 70:30 at different conditioning periods (Figure 5.5) which showed that there was no difference in release rate with conditioning periods of 96 hours and 1 month. The results are consistent with the continuous-flow experiments where there was considerable activity in the first three days (increasing release rate) after which time the bulk water concentration decreases to a steady-state. Therefore, the results from the linear polarization studies support the results from the release rate studies using conditioned plates.
The copper release rate results for the copper-nickel alloys were compared to the zebra mussel recruitment observations of Dormon et al. (1996) (see Table 5.5). The results showed that zebra mussels did not attach to Cu:Ni 90:10 which had a similar release rate to copper (27.7 mg·m⁻²·day⁻¹). A few mussels were found on Cu:Ni 80:20 and larger amounts recruited to Cu:Ni 70:30, both of which had significantly lower copper release rates compared to copper and Cu:Ni 90:10. These results suggest that the prevention of zebra mussel biofouling corresponds to increasing copper release rates. Therefore, it is important to optimize the antifouling characteristics of the copper-nickel alloys and their inherent copper release rates in order to prevent biofouling using materials which have low copper release rates. In addition, cost and suitability of the material to the application must also be considered.

Although these results suggest that copper release rate is the active mechanism preventing zebra mussel attachment, a conclusion cannot be made until it has been shown that the surface properties of the copper alloys do not contribute to the anti-fouling mechanism of these materials. The topic of the next Chapter addresses the potential of the copper surfaces to prevent biofouling.
Table 5.5: Zebra Mussel Biofouling on Copper Materials (from Dormon et al., 1997)

<table>
<thead>
<tr>
<th>Material</th>
<th>Deployment Time (months)</th>
<th>Number of Mussels (number per m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>0</td>
</tr>
<tr>
<td>Cu:Ni 90:10</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>112</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>11</td>
</tr>
<tr>
<td>Cu:Ni 70:30</td>
<td>15</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>250</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>9000</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>3000</td>
</tr>
</tbody>
</table>
5.5 Summary

Under batch experimental conditions, the bulk copper concentration released from the copper-nickel alloys builds up to a meta-stable supersaturated point which suppresses further release of copper and with increasing time, the copper concentration decreases to a new level as was observed using copper plates. These results indicated that batch experimental conditions do not provide an accurate measure of copper release into fresh lake water that would be observed under natural conditions.

As the copper composition of the copper-nickel alloys decreases, the copper and nickel release rates decrease. This may be explained by the existence of the more protective oxide layer that is formed on copper-nickel alloys containing larger amounts of nickel. This decrease in release rate with increasing nickel alloy content also corresponded to an increase in the polarization resistance.

The release of copper and nickel from copper-nickel alloys can be described using the copper release rate model for the reaction-limited regime under continuous-flow conditions. The ratio of the copper release rate to the nickel release rate approximately corresponded to the mass ratio in the material. In addition, the residence times required to reach steady state for copper and nickel from the same alloy were similar which again indicate that the copper and nickel are released into solution in proportion to the alloy composition but at similar rates.
Conditioning times of 96 hours and 1 month prior to testing resulted in the same copper and nickel release rates. This was consistent with the linear polarization measurements which showed that after three days the corrosion rate of the surface was constant. This indicates that the copper-rich layer which builds up on the alloys during different times of conditioning is easily removed when exposed to fresh lake water conditions and allows the surface to release again at the same rate as a sample which had been conditioned for a shorter time.
Chapter 6

Understanding the Anti-fouling Mechanism of Copper-Containing Materials

6.1 Introduction

As discussed in Chapter 2, two mechanisms have been proposed to explain the anti-fouling characteristics of copper: the release of copper versus surface phenomena (Boyer and Gall, 1985; Swain et al., 1982). The anti-fouling characteristics of copper release as a corrosion by-product have been attributed to the corrosion species' toxic nature which inhibits biofouling (Swain et al., 1982). Other investigators have speculated that copper surface properties i.e., oxide, prevent attachment (Wentzell, 1993). The majority of work on this topic has been performed in the marine environment and the anti-fouling mechanisms of copper in fresh water have not been examined.

The discussion in previous Chapters indicated that higher copper release rates were directly related to the reduction in zebra mussel recruitment. A comparison of previous recruitment results conducted at a Lake Erie field site (Dormon et al., 1997) with copper release rates from the acid-etched copper and copper-nickel alloys, used in those studies, indicated that reductions in zebra mussel biofouling corresponded to higher copper release rates. These findings suggested that copper release rate (i.e., cupric ions) prevented zebra mussel biofouling but did not disprove the theory that the surface properties of the copper-containing materials prevented zebra mussel attachment.

In order to test the hypothesis that the anti-fouling nature of the copper-containing materials was not related to the surface characteristics of these substrates, experiments were designed to investigate the surface properties and copper release rates of materials which
prevented zebra mussel biofouling. The materials used in these experiments included: copper galvanic couples, copper-epoxy, and copper and copper-nickel alloys which had been conditioned in Lake Erie for five years. A comparison of the surface characteristics and copper release rates of these materials with the results from the release rates from previous Chapters and recruitment observations was done to elucidate the mechanism by which copper-containing materials prevent zebra mussel attachment.

The goal of this Chapter is to compare the surface characteristics and copper release rates from the various materials which have been shown to reduce zebra mussel recruitment in order to determine the mechanism which is active in biofouling prevention. The results from this Chapter were used to answer Objective 3 of the thesis, namely;

- To identify the physical and chemical characteristics of copper and copper-nickel alloys that give rise to biofouling resistance.

6.2 Methods and Materials

6.2.1 Lake Erie Conditioned Copper Alloys

In order to determine long-term lake water conditioning effects on the copper release rates and surface characteristics of copper-containing alloys, copper and copper-nickel alloys (Cu:Ni 90:10, 80:20, and 70:30) that had been placed into Lake Erie in the summer of 1991 were removed for testing. Once the plates (8 cm x 16 cm x 0.16 cm) were removed from the lake, recruitment or zebra mussel attachment observations were recorded. After the five years of lake water exposure the copper and Cu:Ni 90:10 surfaces were covered with a thick biofilm and a few mussels were attached to the biofilm but not directly to the metal surface.
However, the Cu:Ni 70:30 surface was covered by biofilm and mussels were found attached to the metal surface. Following the recruitment counts, the copper alloys were lightly sprayed with Lake Erie water to remove the biofilm from the surface. The plates were then placed into separate low-density polyethylene (LDPE) bags filled with approximately 15 mL of Lake Erie water and placed into a cooler for transport to the laboratory. One plate of each material was cut into sample pieces (2 cm x 1 cm) and then used for X-ray photoelectron spectroscopy (XPS), X-ray diffraction, and scanning electron microscopy (SEM) analyses for comparison of the surface oxide products. The remaining conditioned plates were used in the copper release rate studies.

6.2.1.2 X-ray Photoelectron Spectroscopy (XPS) Studies

The conditioned copper alloy plates were cut into 2 cm$^2$ pieces using a metal shear and sent to Dr. T. DeBies at XEROX, Webster, New York for XPS analysis. A full description of the XPS analytical method is included in Appendix C. The electron spectra were measured using a Kratos XSAM 800 Electron Spectrometer. The copper alloy samples were irradiated with Al ka X-rays at a power of 300 Watts (15 kV, 20 mA). The spectrometer was calibrated with references to the Au 4f$^{7/2}$ line at 84.0 eV and the Cu 2p$^{3/2}$ line at 932.6 eV. Using these references, the binding energy of the C 1s hydrocarbon line for hydrocarbon contamination on a gold substrate is 284.8 eV.
6.2.1.3 X-ray Diffraction Studies

The conditioned copper alloy plates were cut into 2 cm² pieces using a metal shear and sent to Dr. S. Petrov at the Department of Chemistry, University of Toronto, Toronto, Ontario for X-ray diffraction analysis.

6.2.1.4 Scanning Electron Microscopy (SEM) Examination

The conditioned copper alloy plates were cut into 1 cm² pieces using a metal shear and then sent to Fred Neub of the Department of Metallurgical and Materials Engineering for sample preparation and SEM analysis. The copper alloy plates were first embedded in a carbon epoxy and then the surface was lightly polished using 1μm Al₂O₃. The samples were then viewed using SEM S-520.

6.2.1.5 Release Rate Studies

Once the conditioned plates were returned to the laboratory, they were immediately placed into aerated, filtered Lake Ontario water (0.2 μm, nominal), under dark conditions, overnight. Although spraying removed a substantial amount of the biofilm present on the surface, it was important to ensure that any remaining biofilm was destroyed. This was done to prevent the adsorption of copper from the bulk solution or increased corrosion rates due to biofilm metabolic activity. Therefore, the biofilm remaining on the plates was destroyed using a glutaraldehyde treatment.

The glutaraldehyde treatment procedure was initially tested using the lake water conditioned Cu:Ni 80:20 plates and acid-etched Cu:Ni 80:20 plates were used as a control.
After rinsing the Cu:Ni 80:20 plates with filtered Lake Ontario water, they were submerged in a 2% glutaraldehyde solution for two hours. After the two hour glutaraldehyde treatment, the plates were thoroughly rinsed in Lake Ontario water and then placed into the continuous-flow experimental set-up with filtered lake water (Chapter 4, Figure 4.1) using the procedure described in Chapter 4. The experiment was conducted at a low flow rate of 2 mL·min⁻¹ to obtain copper concentrations above the graphite furnace atomic absorption spectrometry (GFAAS) detection limit. Bulk liquid samples were taken from the outlet port of the vessel at regular time intervals, acidified to a pH < 2, and analyzed by GFAAS. The experiment was continued until the system reached a steady-state copper concentration.

At the end of the Cu:Ni 80:20 experiment, a slimy fungus or yeast was found growing on the surfaces of the plates indicating that either the glutaraldehyde treatment was not appropriate or that contamination had occurred (i.e., some of the lake water used for transporting the plates to the laboratory entered into the vessel). The living biofilm on the plates could have increased corrosion rate due to metabolic activities or adsorbed copper from the bulk solution; both of which would have affected the copper release rate. Therefore, a new technique was required to destroy the biofilm.

Prior to measuring the copper release rate from the remaining lake water conditioned plates, microbiological tests were performed to ensure that the biofilm was destroyed with the glutaraldehyde treatment. Biofilm samples from the surfaces of the alloy plates were taken before and after a two hour treatment with a 3% glutaraldehyde solution. The plates were rinsed with Lake Ontario water and then placed into the continuous-flow experimental set-up.
The experiments were conducted at 8 mL·min⁻¹ for one month and bulk liquid samples were taken at regular time intervals from the outlet port of the vessel, acidified to a pH < 2, and analyzed by GFAAS.

6.2.2 Galvanic Couple Experiments

A continuous-flow system was designed for the galvanic couple experiments to prevent the build-up of copper concentration in the bulk solution which can affect the release rate from copper (see Chapter 4). The system consisted of a 4.2 L plastic vessel equipped with inlet and outlet ports (Figure 6.1). The vessel was fed a continuous-flow of filtered (0.2 μm nominal) Lake Ontario water using a peristaltic pump and water flow rates were determined by measuring the time to fill a volumetric flask. Each vessel contained one galvanic couple having dimensions of 6.3 cm x 18.9 cm which rested at the bottom of the vessel. An air pump connected to LDPE tubing was used to maintain near saturated oxygen conditions within the vessel.

Copper plates (6.3 cm x 6.3 cm) were coupled with two plates (6.3 cm x 6.3 cm) of aluminum (Cu-Al) in one system and zinc (galvanized steel; Cu-Zn) in the other. A copper-copper (Cu-Cu) couple was used as a control. The couples were connected using copper rivets as shown in Figure 6.1 and then each couple was placed into a separate plastic vessel, described above, containing 1.5 L of filtered Lake Ontario water (0.2 μm nominal). The couples were placed into the vessel and were supported by the rivets to prevent the couples
Figure 6.1: Schematic diagram of the continuous-flow vessel for the galvanic couple experiment, showing the top view (A) and the side view (B).

from touching the bottom and allow lake water to circulate around the couple. A flow rate of 5 mL·min⁻¹ of filtered lake water was used throughout the experiment. Liquid samples were taken at the outlet of the vessel after 24 hours and at the end of the experiment (seven days), acidified to a pH < 2, and analyzed for copper content using GFAAS.

At the end of the experiment, the couples were removed from the vessels and prepared for XPS analysis. Samples were cut from the copper portion of the couples using a metal shear.
The samples were cut from a position nearest the connection point of the copper plate and the coupled metal as well as from the middle section of the copper plate. The two positions were selected in order to determine whether there was a difference in oxide species with distance from the coupling and also to observe whether plating occurred over the copper part of the couple. The samples were sent for XPS analysis as in Section 6.1.1.2.

In order to investigate the characteristics of copper connected in a galvanic couple under short-term exposure conditions, the galvanic couple experiment was repeated. Copper (5.5 cm x 5.5 cm) was coupled with two plates (5.5 cm x 5.5 cm) of zinc (galvanized steel; Zn) using copper rivets. The couple was placed into 1.5 L of aerated, filtered Lake Ontario water in the test vessel described above and maintained under stagnant conditions for 1 hour. This experiment was done to replicate previous laboratory studies in which mussel response to contact with copper in a galvanic couple under stagnant conditions was investigated.

At the end of the experiment, samples from the copper plate portion of the couple were cut from the edge and middle positions, described above, using the metal shear. The samples were sent for XPS analysis as in Section 6.1.1.2.

6.2.3 Copper Release Rate from Copper-Epoxy

Four copper-epoxy (Hi-Tek Manufacturer:copper particles (99.9 % pure, comprised of 66 % by weight) embedded in an epoxy matrix) plates (8 cm x 15.5 cm) were cleaned with ethanol, allowed to dry, and then placed into the polytetrafluoroethylene (PTFE; Teflon) holders in the continuous-flow experimental set-up (Chapter 4, Figure 4.1) containing 1 L of filtered, Lake Ontario water (0.2 μm nominal). The experiment was conducted at a flow rate
of 8 mL·min⁻¹. Liquid samples were taken at regular time intervals near the outlet port of the vessel, acidified to a pH < 2, and analyzed for copper concentration using GFAAS. The experiment was continued until the copper concentration reached a steady-state.

6.3 Results

6.3.1 Lake Water Conditioned Plates

6.3.1.1 Surface Studies

A comparison of the oxide species present on the five year lake water conditioned copper and copper-nickel plates is shown in Table 6.1. XPS analysis of these plates showed the presence of carbon, calcium, silicon, and nitrogen due to the thick biofilm layer on the surface. The results showed that three copper oxide species were present on the Cu:Ni 90:10 surface: Cu₂O (69.74%), CuO (20.57%) and Cu(OH)₂ (9.69%). Two oxide components were detected on the Cu:Ni 70:30 surface: Cu₂O (72.40%) and CuOH⁺ (27.60%). The oxide species present on the copper surface were CuO (61.6%) and Cu(OH)₂ (38.4%).

There was no difference on the conditioned copper alloy surfaces examined by X-ray diffraction. The results from these analyses indicated that the oxide present on the surfaces of the copper, Cu:Ni 90:10, and Cu:Ni 70:30 plates was Cu₂O.
Table 6.1a: Elemental species from XPS survey of lake water conditioned plates. (Note: numbers are atomic percentages)

<table>
<thead>
<tr>
<th>Element</th>
<th>Copper</th>
<th>Cu:Ni 90:10</th>
<th>Cu:Ni 70:30</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>51</td>
<td>47</td>
<td>54</td>
</tr>
<tr>
<td>O</td>
<td>39</td>
<td>41</td>
<td>37</td>
</tr>
<tr>
<td>Cu</td>
<td>2</td>
<td>2</td>
<td>0.6</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>N</td>
<td>3</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>-</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>Si</td>
<td>4</td>
<td>4</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6.1b: XPS results of oxide species on the surfaces of the conditioned copper plates. (Note: numbers are concentration percentages)

<table>
<thead>
<tr>
<th>Species</th>
<th>Copper</th>
<th>Cu:Ni 90:10</th>
<th>Cu:Ni 70:30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₂O</td>
<td>-</td>
<td>69.7</td>
<td>72.4</td>
</tr>
<tr>
<td>CuOH⁺</td>
<td>-</td>
<td>-</td>
<td>27.6</td>
</tr>
<tr>
<td>CuO</td>
<td>61.6</td>
<td>20.6</td>
<td>-</td>
</tr>
<tr>
<td>Cu(OH)₂</td>
<td>38.4</td>
<td>9.7</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 6.2: SEM photos of the lake water conditioned copper alloys showing the oxide layer thickness for (top) copper, (middle) Cu:Ni 90:10 and (bottom) Cu:Ni 70:30.
The thickness of the oxide layers on the lake water conditioned copper and copper-nickel plates was measured using SEM (Figures 6.2a, b, and c). Two distinct layers were found on the conditioned surfaces and both were included in the thickness measurement. The thickest layer was observed on Cu:Ni 90:10 having a value of 150 μm whereas copper and Cu:Ni 70:30 had similar oxide thicknesses of 15 μm.

6.3.1.2 Copper Release Rates

A comparison of the copper release rates from acid-etched, glutaraldehyde treated and untreated copper-nickel 80:20 plates (Figure 6.3) indicated that the copper release rates at the transient (the time before reaching steady-state) period of the release rate curve were lower for the plates which had the glutaraldehyde treatment and steady-state was achieved in a shorter time. However, the steady-state copper release rate, which is of primary interest in these experiments, was not altered by the treatment. Therefore, the glutaraldehyde treatment was used to prepare the lake water conditioned plates for the remaining release rate studies.

The copper release rates from the lake water conditioned Cu:Ni 80:20 plates were compared with those from acid-etched Cu:Ni 80:20 (Figure 6.4) and the results showed that the release rate increased from 5 mg·m⁻²·day⁻¹ for freshly etched plates to 10 mg·m⁻²·day⁻¹ after five years of lake water exposure. As mentioned in the previous section, a fungus or yeast was found growing on the plate surfaces which may have contributed to the increased release rate.

The results from the three remaining lake water conditioned plates were compared. The copper concentrations for the three lake water conditioned copper alloys (Cu, Cu:Ni
90:10, and Cu: Ni 70:30) increased to their steady-state values; achieving these values after approximately 150 hours. The corresponding copper release rates were obtained by substituting the copper concentration values into the reaction limited continuous-flow equation (Equation 4.8) and the results are shown in Figure 6.5. The ranking of copper release rate was copper > Cu: Ni 90:10 ≈ Cu: Ni 70:30 which corresponded to values of 26 mg m⁻² day⁻¹, 19 mg m⁻² day⁻¹ and 19 mg m⁻² day⁻¹, respectively.

6.3.2 Galvanic Couples

The results from the analysis of the bulk liquid samples from the galvanic couple experiments (Table 6.2) show that the copper-copper couple released copper into solution at comparable rates to copper under continuous-flow conditions (See Chapter 4). However, the copper release rates from the copper plates coupled with either aluminum or zinc was significantly reduced and analysis by GFAAS (detection limit 0.4 μg L⁻¹) showed that the concentrations were not different from the lake water copper concentration. This result confirms that the copper release rate was suppressed by electrically connecting copper to a less noble metal.

Table 6.2: Results from GFAAS analysis of bulk water from the galvanic couple experiments. (Note: values are copper concentrations (unit mg L⁻¹), background copper concentrations have been subtracted)

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Cu-Cu</th>
<th>Cu-Zn</th>
<th>Cu-Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.1</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
<tr>
<td>7</td>
<td>62.6</td>
<td>&lt; DL</td>
<td>&lt; DL</td>
</tr>
</tbody>
</table>
X-ray photoelectron spectroscopy analysis of the copper surfaces showed that the copper surface in contact with the zinc plate was covered with a zinc film. Similarly, the copper connected to the aluminum plate was covered with an aluminum film. Further analysis was done using energy dispersive X-ray analysis (EDAX) to determine whether the films were uniform over the surfaces of these copper plates. The EDAX analysis indicated that the surface of copper coupled with zinc was covered with a zinc film except for some patches, approximately 100 μm in length, that did not have zinc present. The analysis showed that the copper coupled with aluminum plates had smaller areas which were predominantly copper but that the surface was mostly covered with aluminum.

In order to provide an accurate surface analysis of the copper oxides on the copper plates and prevent plating from the anodic metal, the galvanic couple experiment was repeated under stagnant conditions for one hour and the copper plate was analyzed by XPS. A comparison of the XPS results for the copper plates from the couples (Table 6.3) shows that the species present on the copper surface whether coupled with copper or zinc were the same although the percentages of these species were slightly different. The oxide species on the copper plates which were coupled with zinc were predominantly the less oxidized form. This may have been the result of the shorter duration of the copper-zinc couple experiment.
Figure 6.3: Effects of glutaraldehyde treatment on the copper release rate from acid-etched Cu:Ni 80:20 plates.
Figure 6.4: Comparison of copper release rates from lake conditioned and acid-etched Cu:Ni 80:20 plates. (Error bars are the standard errors of replicate results (n=2) from the analysis of each water sample). Note: some errors are smaller than the symbol size.
Figure 6.5: Comparison of copper release rates from lake water conditioned plates at a flow rate of 8 mL·min⁻¹.
6.3.3 Copper-Epoxy Release Rate

The copper concentrations in the bulk solution from the experiments using copper-epoxy plates were converted into copper release rates using Equation 4.19 and the results were compared to the release rates from freshly etched copper plates (Figure 6.6). The initial steady-state copper release rate from the copper-epoxy was similar to the release rate from the copper plates (approximately 26 mg m\(^{-2}\) day\(^{-1}\)), although the transition phase to steady-state was slightly lower. After approximately 200 hours of continuous-flow exposure there was an increase in copper release from the copper-epoxy up to a value of 40 mg m\(^{-2}\) day\(^{-1}\) which was not observed for dissolution from the copper plates.

Table 6.3: XPS results for the oxide species present on the copper plates of the galvanic couples.

<table>
<thead>
<tr>
<th>Species</th>
<th>Cu-Cu</th>
<th>Cu-Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)O</td>
<td>57 %</td>
<td>74 %</td>
</tr>
<tr>
<td>CuO</td>
<td>25 %</td>
<td>17 %</td>
</tr>
<tr>
<td>Cu(OH)(_2)</td>
<td>18 %</td>
<td>9 %</td>
</tr>
</tbody>
</table>
Figure 6.6: Copper release rate from copper-epoxy compared with release from copper.
6.4 Discussion

The glutaraldehyde treatment was a reliable method for destroying the biofilm on the surfaces of the lake water conditioned plates and did not affect the copper release rate. A comparison of the copper release rates from glutaraldehyde treated and untreated acid-etched Cu:Ni 80:20 plates (Figure 6.3) showed that the steady-state copper release rates were the same. However, the transition to the steady-state point was not identical for both treatments. Since the values of interest, the steady-state points, were similar for both treatments, the glutaraldehyde solution was considered for preparing the remaining lake water conditioned plates prior to the release rate studies. Microbial tests confirmed that increasing the glutaraldehyde treatment to 3% effectively destroyed the biofilm. Since the glutaraldehyde treatment was effective and did not affect the steady-state copper release rate, the treatment was used to treat the remaining conditioned plates before testing.

The copper release rates from the glutaraldehyde-treated lake water conditioned copper and copper-nickel plates were either greater than or equal to the results from the same alloys after acid-etching (Figure 6.5). This is in contrast to results from other investigations (Reiber et al., 1987, Stone et al., 1987) that have shown that copper corrosion decreases with the time of exposure. The copper release rates from the lake water conditioned copper and Cu:Ni 90:10 plates were similar to the values from the corresponding acid-etched plates. This result indicated that the release rates from the higher copper-containing alloys did not change significantly during the five year exposure period. However, copper release rates from the lake water conditioned Cu:Ni 80:20 and Cu:Ni 70:30 increased after five years of
exposure. In the previous section, the increased copper release rate from the Cu: Ni 80:20 plates was the result of the biofilm growing on the plates during the experiment. The metabolic activity of the biofilm on the metal surface can increase the corrosion rate of the copper-nickel plates resulting in a greater copper release rate (Davidson, 1995). However, this does not explain the larger copper release rate from Cu: Ni 70:30 after five years of lake water conditioning since microbial tests had shown that the 3 % glutaraldehyde solution destroyed the biofilm.

Although the biofilm on the conditioned plates had been killed, large dead portions remained attached to the copper alloy surfaces and entered into the vessels with the plates, producing the increased copper release rates. This increase in copper release rate can occur in two ways. Firstly, studies (Mittelman and Geesey, 1985) have shown that the constituents of biofilms can adsorb copper and produce increased dissolution rates when active. When the same biofilm has been destroyed, it can fall off the surface of the metal. Once the biofilm sloughs off the surface, it enters into the bulk phase increasing the bulk copper concentration (Davidson, 1995). An investigation conducted by Mittelman and Geesey (1985) was done to determine the copper-binding capacity of a freshwater-sediment bacterium. They found that the maximum binding capacity of a purified exopolysaccharide would range from 62 to 253 nmol of copper per mg of carbohydrate. Assuming that the amount of copper adsorbed by the biofilm on the conditioned plates used in the present study was similar to that determined by Mittelman and Geesey (1985) and that a 5 mm thickness of biofilm was present on the plates, then the difference in copper release rate from Cu: Ni 70:30 acid-etched and conditioned
surfaces can be explained by the continuous loss of copper from the biofilm to the bulk water. The dead biofilm remaining on the copper alloy surfaces may have also contributed to the increased copper release rates from the conditioned surfaces. Biofilms can inhibit the diffusion of reactants or products involved in the corrosion processes on the metal surface leading to the formation of concentration cells which further increases the rate of copper dissolution and impedes the formation of an oxide layer (Davidson, 1995). It can be concluded that the presence of a biofilm causes sustained corrosion for prolonged periods of time (Webster et al., 1996). The presence of the biofilm suggests the cause of the large copper release rates from the copper-nickel alloys after five years of lake water exposure.

Surface analysis of the conditioned copper and copper-nickel alloys indicated that there was no difference in oxide products among the copper-containing materials. It was difficult to obtain conclusive results from the XPS analysis due to the thick biofilm present on the surface of the conditioned plates and the large amounts of carbon, calcium, silicon, and nitrogen. However, various oxides on the surfaces of the lake water conditioned plates were identified. X-ray diffraction analysis indicated that Cu$_2$O was the only oxide product present on the conditioned copper and copper-nickel plates. The discrepancy between the results obtained using XPS and X-ray diffraction may be due to the shallower sensing depth of the X-ray diffraction technique in comparison with XPS.

The thickness of the oxide layers was measured using SEM. The results from SEM indicated that the thickest oxide layer, 150 $\mu$m, was on Cu:Ni 90:10. The thickness of the oxide layers on copper and Cu:Ni 70:30 had similar values of 15 $\mu$m. This trend in relative
thickness values is similar to the results obtained by North and Pryor (1970) who measured the thicknesses of the oxide layers formed on copper and copper-nickel alloys which had been immersed in a 3.4 % NaCl solution. North and Pryor explained that the thicker oxide layer on the Cu:NI 90:10 alloy was the result of the nickel in the alloy stabilizing the oxide (i.e., Cu₂O) against dissolution whereas the thinner oxide layer on the Cu:Ni 70:30 plates was the result of its very high resistivity.

The second material examined to determine the anti-fouling mechanisms of copper-containing materials was copper embedded in an epoxy matrix. Initially, the copper release rate from the copper-epoxy was similar to that from the acid-etched copper. However, after approximately 200 hours of continuous-flow exposure, the copper release rate from the copper-epoxy rose rapidly away from the steady-state point. In order to explain the rapid increase in copper release rate, the bulk solution remaining at the end of the experiment was examined. The solution was filtered through a 0.45 μm filter and then the filter paper was dried and examined using EDAX. The results from EDAX showed the presence of copper and silica particles which suggested that the epoxy material was dissolving in the lake water and releasing the copper particles. The copper particles from the copper-epoxy have a larger surface area available for dissolution which increases the copper content in the bulk water. In addition, the particles of copper released from the copper-epoxy could have been included with the bulk liquid samples and included in the GFAAS analysis, increasing the copper concentration of the sample. The combination of these two factors account for the increase in copper release rate from the copper-epoxy past the steady-state point.
The final group of materials examined in this Chapter were the copper couples. XPS analysis of the copper surfaces which had been joined with either copper or zinc indicated that the surface oxide species were the same on both. The copper surfaces connected to either copper or zinc had Cu$_2$O present in the greatest amount followed by CuO and then Cu(OH)$_2$. The percentages of oxide species present on the two surfaces were not exactly the same due to either the longer duration of the copper-copper couple experiment or the XPS curve fitting routine, but the relative amounts of the oxide species were similar. The results from the GFAAS copper analysis of the bulk liquid showed that although the copper-copper couple released copper at rates similar to those from etched copper plates, the coupling of copper with zinc suppressed copper release to a level below the detection limit of GFAAS. These results can be directly related to the zebra mussel recruitment observations.

A comparison of the characteristics of the materials examined in this Chapter indicate that copper release rate is directly related to the anti-fouling characteristics of the copper-containing materials. First, the zebra mussel recruitment observations (Dorman et al., 1997) showed that zebra mussels did not recruit onto copper and Cu:Ni 90:10, but mussels were found attached to Cu:Ni 70:30. Even after five years, the anti-fouling capabilities of these materials had not been altered by lake water exposure. Comparing these recruitment observations to the copper release rates from the conditioned copper and copper-nickel plates shows that the prevention of attachment is directly related to higher copper release rates. Surface analysis confirmed this speculation by showing that the oxide species on the copper and copper-nickel plates were all of the same form, Cu$_2$O. These studies show that the only
difference in the characteristics of these conditioned alloys is the copper release rate. However, recruitment studies indicate that zebra mussels have different preferences for these materials. Therefore, copper release rate is the active mechanism which prevents zebra mussel attachment.

The galvanic couple experiments also show that copper release rate prevents zebra mussel attachment. Recruitment studies have shown that when copper is coupled with either zinc or aluminum, zebra mussels attach to the copper plate section of the couple (Dormon et al., 1996). When copper was coupled with zinc, the copper release rate was substantially reduced but the copper oxide species present on the copper plate were similar to those on copper coupled with copper. Therefore, the only difference between the characteristics of the copper-copper couple and the copper-zinc couple was copper release rate. This result again supports the hypothesis that copper release prevents zebra mussel attachment.

Finally, the results from the studies using the copper-epoxy confirm that copper release rate prevents zebra mussel attachment. An examination of previous recruitment observations (Dormon et al., 1996) indicates that copper-epoxy prevents zebra mussel attachment to a similar extent as the higher copper-content surfaces (0 mussels per m² attached after 15 months and 89 mussels per m² attached after 26 months, Dormon et al., 1997). The copper release rate from the copper-epoxy was similar to the copper release rate from the acid-etched copper. Since the surface of the copper-epoxy consists of patches of epoxy and copper, it is not a continuous surface. Therefore, the uniform copper oxide layer that forms on a copper plate surface would not form on the copper-epoxy surface; suggesting
that copper release rate is the only similar feature of the two materials. This result also supports the hypothesis that copper release rate is the mechanism by which copper-containing materials prevents biofouling because the two materials prevent attachment and release copper at similar rates.

The results from this Chapter agree with the proposed mechanism for copper anti-fouling in marine environments. Several other studies (Boyer and Gall, 1985; Swain et al., 1982) suggest that the anti-fouling mechanism of copper materials in sea water is due to the leaching of toxic copper ions from the surface. Therefore, the anti-fouling mechanism of copper and copper-nickel alloys is similar in marine and freshwater environments.

6.5 Summary

The 3% glutaraldehyde treatment provided an effective method for destroying the biofilm present on the Lake Erie conditioned copper alloy plates.

Previous laboratory and field studies have shown that when copper is galvanically coupled with either aluminum or zinc, zebra mussels attached to the copper component of the couple. The results from this Chapter clearly show that the copper release rate is significantly decreased when placed in a galvanic couple with zinc or aluminum. This leads to the conclusion that copper release is the active mechanism in the prevention of zebra mussel biofouling.

The copper release rates from lake water conditioned copper and Cu: Ni 90:10 and 70:30 were either equal to or greater than the release rates from the same alloys having etched surfaces. This observation was the result of the presence of the biofilm on the surfaces of the
copper-alloy plates which either enhanced the dissolution process or fell off the surface and increased the bulk liquid copper concentration.

X-ray diffraction analysis showed that the oxide products on the conditioned copper and copper-nickel surfaces were the same, i.e., Cu₂O. The oxide layer was the thickest on Cu:Ni 90:10 and the oxide layers on copper and Cu:Ni 70:30 were similar and a factor of ten times thinner than the thicker oxide layer. These results agree with the work of North and Pryor (1970) which can be used to explain the difference in release rate between the different copper alloys.

The oxide products on copper coupled with zinc were the same as those on copper coupled with copper. The copper release rates were suppressed when copper was coupled with zinc.

Copper-epoxy had similar copper release rates to those of acid-etched copper. However, with longer exposure periods the copper release rate doubled. This was the result of the epoxy material dissolving in the bulk water and releasing the copper particles into solution.
Chapter 7

Summary

The work in this thesis examined different materials for controlling zebra mussel biofouling in industrial applications i.e., piping systems, valves. Current control strategies are either very costly and labour intensive or pose potentially harmful environmental impacts. Before materials could be suggested for biofouling control, a better understanding of zebra mussel adhesion was necessary. This was achieved by considering two aspects of zebra mussel attachment: (i) the strength with which zebra mussels attach to various substrates, and (ii) the prevention of attachment to certain materials.

In the first part of this work, a wall-jet apparatus was designed to measure the adhesion strength of zebra mussels which had recruited onto materials exposed in Lake Erie (Chapter 3). The wall-jet and direct pull-off tests indicated that the lowest attachment strength was on Teflon, whereas mild steel required the greatest mean force to remove the attached mussels. Attachment strength increased with increasing surface roughness, probably as a result of increased mechanical interlocking of the zebra mussel plaques with the substrates. These results suggest that material selection can enhance cleaning efforts by decreasing the attachment strength. While material selection can enhance cleaning efforts, the cleaning process is still very costly and labour intensive. Although the zebra mussel can be removed from a surface, the byssal threads can remain on the surface and this has in some cases lead to increased corrosion rates of the material. Therefore, a material which prevents zebra mussel attachment is ideally desired.
Previous recruitment studies showed that copper and, to a lesser extent, copper-nickel alloys prevent zebra mussel attachment (Dormon et al., 1997). The anti-fouling characteristics of copper have been known in the marine environment for many years and were attributed to the release of cupric ions. However, little information was known about the anti-fouling behaviour of copper in fresh water. In order to compare the copper release rates from various copper-containing materials, the initial copper dissolution values were desired. Two experimental systems were designed for the release rate experiments: batch and continuous-flow conditions. Batch experimental conditions did not provide an accurate measure of copper release rate because the build-up of copper within the bulk water suppressed the initial copper release rate and resulted in the precipitation of copper complexes. Continuous-flow experimental conditions provided a better evaluation of the initial copper release rate into natural lake water which has a low background copper concentration.

Although the batch experiments were not appropriate for this work, their application should not be overlooked. For example, the results can be used to quickly predict copper concentrations under stagnant conditions such as in heat exchangers and piping.

Copper release rates from copper and copper-nickel alloys into fresh water were described using a comprehensive model which described the initial dissolution process under continuous-flow conditions as being controlled by reaction-limited conditions.

Generally, initial copper release rates increased with increasing copper content of the alloy. A comparison of initial copper release rates from acid etched copper and copper-nickel alloys showed that copper and Cu:Ni 90:10 had the greatest copper release rates;
26 mg m\(^{-2}\) day\(^{-1}\) and 28 mg m\(^{-2}\) day\(^{-1}\), respectively. Copper release rates from Cu:Ni 80:20 and Cu:Ni 70:30 were 5.3 mg m\(^{-2}\) day\(^{-1}\) and 1.8 mg m\(^{-2}\) day\(^{-1}\), respectively.

In contrast to the copper release rate results, initial nickel release rates decreased with increasing nickel content of the alloy. A comparison of the initial nickel release rates from acid etched copper-nickel alloys showed that the nickel release rate from Cu:Ni 90:10 was 5.2 mg m\(^{-2}\) day\(^{-1}\), from Cu:Ni 80:20 it was 1.5 mg m\(^{-2}\) day\(^{-1}\), and from Cu:Ni 70:30 it was 0.8 mg m\(^{-2}\) day\(^{-1}\). The ratio of the copper release rate to the nickel release rate approximately corresponded to the mass ratio in the material.

The results from the linear polarization method supported the trends obtained in the copper release rate experiments. The polarization resistance curve obtained for Cu:Ni 70:30 had the greatest slope, or lowest corrosion rate, whereas Cu:Ni 90:10 had the lowest slope, and therefore the highest corrosion rate. The ranking of corrosion rates determined using linear polarization was consistent with the ranking of copper release rates from the copper-nickel alloys.

In addition, linear polarization was used to monitor the change in oxide layer growth or corrosion rate with time of exposure to lake water. After a period of approximately 30 days, a comparison of the results from the polarization studies and the release rate experiments showed that in the first 3 - 10 days there was a lot of activity in both the copper release rates and the polarization resistance values after which time the values remained constant.

A comparison of the characteristics of copper-based materials and their anti-fouling performance indicated that the copper release rate correlated with the prevention of zebra
mussel attachment. Suppressing the copper release rate, by electrically connecting copper plates to less noble materials in a galvanic couple, eliminated copper's anti-fouling characteristics as shown by the recruitment of zebra mussels onto the surfaces of the copper plates (Dormon et al., 1997). Since the other surface characteristics of the copper plate in contact with zinc were similar to those of freely-corroding copper plates, these studies confirmed that copper release prevents zebra mussel attachment.

In order to put the copper release rate from copper plates exposed to fresh water into perspective, these values were compared with naturally occurring copper release rates. An examination of the flux of copper per unit area of drainage basin was conducted by Boyle (1979). The flux values ranged from $8.7 \times 10^{-4}$ mg m$^{-2}$day$^{-1}$ to 0.03 mg m$^{-2}$day$^{-1}$ which are lower than the copper release rates found in this work. The flow rate through the basins was approximately $10^3$ m$^3$s$^{-1}$, which is significantly higher than the flows used in these experiments and provide a greater dilution factor for the copper release rates. In addition, Boyle speculated that the lower copper release rates from the basin may be the result of upper layers protecting the lower copper-containing layers during weathering and mixing events. At the higher dilution rates occurring in the basins, the release rates determined in this work would be much lower.

Another study which examined naturally occurring copper levels found that the copper dissolution rate from inorganic sediment (1300 - 3800 mg Cu kg$^{-1}$) was responsible for 60 mg Cu L$^{-1}$ found in lake water (Spear and Pierce, 1979). This result is approximately one order of magnitude lower than the highest steady-state copper release rate determined under continuous-flow experimental conditions in this study. However, under the laboratory
conditions in this work, the dilution factor was much lower than that occurring naturally. Therefore, the release rates obtained through this work, on a concentration basis, should be lower under natural conditions.

The results from these studies indicate that under natural lake water conditions the copper release rate should be comparable to natural copper release rates. However, the ideal anti-fouling material should consist of an optimal combination of low copper content (i.e., low copper release rate) and maximum biofouling prevention. Further studies can be conducted using the copper concentrations and release rates found in this work to determine copper speciation under these conditions.
Chapter 8

Conclusions and Recommendations for Future Work

8.1 Conclusions

1. The newly designed wall-jet apparatus provided a useful technique for the measurement of zebra mussel adhesion strength and the observation of the events preceding the detachment of the mussel. Preston-static tube measurements were required to provide a more accurate assessment of the shear stress values at the point of mussel attachment because the shear stress values were not uniform over the surface of the test plate.

2. The results from the adhesion strength tests showed that there was a significant difference in attachment strength among the materials tested in this work, ranging from 0.002 Pa m$^2$ to 0.012 Pa m$^2$ using the wall-jet apparatus and ranging from 0.183 N to 1.606 N using the tensile load technique. The adhesion strength of zebra mussels was lowest on smooth Teflon surfaces as shown by testing using the wall-jet apparatus ($0.002 \pm 0.000$ Pa m$^2$) and the spring scale ($0.183 \pm 0.037$ N). The attachment strength of zebra mussels increased significantly with surface roughness on Teflon and stainless steel. A comparison of the two test methods indicated that the adhesion strength results from the tensile load tests were consistent with those from the wall-jet apparatus.

3. A comparison of the characteristics of copper-nickel alloys and their anti-fouling performance indicated that the copper release rate correlated with the prevention of zebra mussel attachment.
4. Under continuous-flow conditions, copper release rates from copper, Cu:Ni 90:10, Cu:Ni 80:20 and Cu:Ni 70:30 into Lake Ontario water (typically pH = 8.17 ± 0.08, temperature = 22 ± 1 °C and saturated oxygen conditions) were 25.8 mg m⁻²·day⁻¹, 27.7 mg m⁻²·day⁻¹, 5.3 mg m⁻²·day⁻¹, and 1.8 mg m⁻²·day⁻¹, respectively. Under continuous-flow conditions in Lake Ontario water (typically pH = 8.17 ± 0.08, temperature = 22 ± 1 °C and saturated oxygen conditions) the nickel release rate from Cu:Ni 90:10 was 5.2 mg m⁻²·day⁻¹, from Cu:Ni 80:20 was 1.5 mg m⁻²·day⁻¹, and from Cu:Ni 70:30 was 0.8 mg m⁻²·day⁻¹.

5. Under low copper concentrations in lake water, the steady-state release rate of copper from a copper containing material is independent of copper concentration and can be represented by the following equation:

\[ k_f = \frac{F(C_{uh} - C_{un})}{A} \]

where \( k_f \) is a constant value.
8.2 Recommendations for Future Work

1. Determine whether the release rate model developed in this work can be used to describe release rates from other metals.

2. Evaluate the copper release rates from copper mesh and screen materials. These materials have been shown to prevent zebra mussel attachment and could provide an alternate material for anti-fouling applications with lower copper release rates.

3. Measure the copper release rates from anti-fouling paints and/or coatings. Other researches have indicated that the anti-fouling mechanism of these paints is due to the copper-oxide composition. A comparison of the copper release rates from these materials with those from copper alloys may provide further insight into the anti-fouling mechanism of the anti-fouling paints.

4. Quantify the copper release rates from other copper alloys, i.e., bronze, copper beryllium, and relate the results to their anti-fouling performance.
Chapter 9

Nomenclature

Symbols used in this thesis

<table>
<thead>
<tr>
<th>Definition</th>
<th>Units</th>
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<tbody>
<tr>
<td>Area of duct</td>
<td>m²</td>
</tr>
<tr>
<td>Projected area for drag force</td>
<td>m²</td>
</tr>
<tr>
<td>Projected area for lift force</td>
<td>m²</td>
</tr>
<tr>
<td>Drag coefficient</td>
<td>-</td>
</tr>
<tr>
<td>Lift coefficient</td>
<td>-</td>
</tr>
<tr>
<td>Copper bulk concentration</td>
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</tr>
<tr>
<td>Inlet copper concentration</td>
<td>mg L⁻¹</td>
</tr>
<tr>
<td>Outer diameter of Preston tube</td>
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</tr>
<tr>
<td>Pressure gradient</td>
<td>kg m⁻² s⁻²</td>
</tr>
<tr>
<td>Hydraulic diameter of the duct</td>
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</tr>
<tr>
<td>Friction factor</td>
<td>-</td>
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<tr>
<td>Water flow rate through copper release rate vessel</td>
<td>mL min⁻¹</td>
</tr>
<tr>
<td>Drag force</td>
<td>kg m s⁻²</td>
</tr>
<tr>
<td>Lift force</td>
<td>kg m s⁻²</td>
</tr>
<tr>
<td>Duct height</td>
<td>cm</td>
</tr>
<tr>
<td>Mussel length</td>
<td>m</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>( p )</td>
<td>Probability</td>
</tr>
<tr>
<td>( P )</td>
<td>Duct perimeter</td>
</tr>
<tr>
<td>( \Delta p )</td>
<td>Difference of total and static pressure</td>
</tr>
<tr>
<td>( \text{Re} )</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>( u_o )</td>
<td>Average velocity</td>
</tr>
<tr>
<td>( (u_o)_B )</td>
<td>Average velocity at bottom of mussel</td>
</tr>
<tr>
<td>( (u_o)_T )</td>
<td>Average velocity at top of mussel</td>
</tr>
<tr>
<td>( u^* )</td>
<td>Kinematic velocity</td>
</tr>
<tr>
<td>( V )</td>
<td>Velocity of fluid</td>
</tr>
<tr>
<td>( x )</td>
<td>Distance from duct opening</td>
</tr>
<tr>
<td>( X^* )</td>
<td>Non-dimensional pressure difference</td>
</tr>
<tr>
<td>( y )</td>
<td>Distance from centreline</td>
</tr>
<tr>
<td>( Y^* )</td>
<td>Non-dimensional shear stress</td>
</tr>
<tr>
<td>( \rho )</td>
<td>Fluid density</td>
</tr>
<tr>
<td>( \tau_w )</td>
<td>Wall shear stress</td>
</tr>
<tr>
<td>( \nu )</td>
<td>Kinematic viscosity</td>
</tr>
</tbody>
</table>
Chapter 10

10.1 References


Dudnikov, V.F. and V.P. Mikheev. The effects of certain metal ions on Dreissena. New York Sea Grant Extension, SUNY, Brockport, N.Y.


Wentzell, J.M. Why copper is anti-fouling. Hi-Tek Chemical Corporation. Hempstead, N.Y.


APPENDIX A

Relationship between wall shear stress and detachment force

The information in this appendix illustrates that the nominal wall shear stress values (obtained for flow over a flat coupon) are approximately proportional to the detachment forces acting on a zebra mussel. The results of Wiberg and Smith (1987), who examined forces on small objects next to a smooth boundary in turbulent flow, are used in deriving the relationship between wall shear stress and detachment force. Wiberg and Smith concluded that lift and drag forces on such objects ($F_L$ and $F_D$ (Newtons), respectively) are proportional to local fluid velocities as follows:

$$F_D \propto \bar{u}^2 \quad [A1]$$

$$F_L \propto (u_T^2 - u_B^2) \quad [A2]$$

In the above expressions, $\bar{u}$ is the average velocity (metres per second) over the height of the mussel given by:

$$\bar{u} = \frac{\int u(z) \cdot dz}{z_T - z_B} \quad [A3]$$

and $z_T$ and $z_B$ are the elevations (metres) of the top and bottom of the mussel, respectively. Similarly, $u_T$ and $u_B$ are the values of $u(z)$ at $z_T$ and $z_B$. For turbulent flow over a flat plate, it is well known that
Appendix A: Relationship Between Wall Shear Stress and Detachment Force

the velocity profile satisfies the log law:

\[
\frac{u(z)}{u^*} = \frac{1}{\kappa} \ln\left(\frac{z}{u^*} \frac{u^*}{v}\right) + b \tag{[A4]}
\]

where \(u^* = \sqrt{\tau_w/\rho}\) is the friction velocity (metres per second), \(\kappa\) is the von Karman constant (=0.41), and \(b\) is a constant (=5). Using Equation [A4], \(F_D\) and \(F_L\) can be evaluated for parameter values typical of flow over a zebra mussel. Specifically, Equations [A3] and [A4] give:

\[
\overline{u} = \frac{u^*}{\kappa(z_T-z_B)} \left\{ z_T^{*} \ln\left(\frac{z_T^{*}}{v}\right) - z_B^{*} \ln\left(\frac{z_B^{*}}{v}\right) \right\} - \frac{u^*}{\kappa} + b'u^* \tag{[A5]}
\]

Using \(z_T=5.0 \times 10^{-3} \text{ m}\), \(z_B=5.0 \times 10^{-4} \text{ m}\), and \(v=1 \times 10^{-6} \text{ m s}^{-1}\), the bracketed term in Equation [A5] varies by only 13 \% for \(\tau_w\) values from 20 to 130 Pa (equivalent to a \(u^*\) variation of 160 \%). Thus, to a good approximation, it is assumed that \(\overline{u}\) is proportional to \(u^*\), so that the drag force \(F_D\) is proportional to \((u^*)^2\), i.e., to \(\tau_w\).

Similarly, the use of Equations [A4] and [A1] and [A2] shows that \(F_L\) is proportional to:

\[
u_T^2 - u_B^2 = \frac{u^{*2} \ln(z_T) - \ln(z_T z_B) + 2 \ln(u^*) - \ln(v) + 2b \kappa}{\kappa^2 z_B}
\tag{[A6]}
\]

The bracketed term is relatively constant, varying by only 13 \% for \(\tau_w\) values in the range of 20 - 130 Pa (equivalent to a \(u^*\) variation of 160 \%). Thus, \(F_L\) is approximately proportional to \((u^*)^2\), i.e., \(\tau_w\).
Since $F_D$ and $F_L$ are both proportional to $\tau_w$, it can be concluded that the net force on a mussel, which is simply the vectorial sum of $F_D$ and $F_L$, is also proportional to the nominal wall shear stress, $\tau_w$.

Finally, it should be pointed out that the derivation presented above has assumed a turbulent velocity profile appropriate for a smooth coupon (Equation [A4]). Coupon roughness will alter the constant in Equation [A4] by an amount proportional to $\varepsilon \cdot u^*/\nu$, where $\varepsilon$ is the nominal coupon roughness. However, for the range of interest in the current study, this does not alter the conclusion that the force on a zebra mussel will be proportional to the nominal wall shear stress, $\tau_w$. 


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<tr>
<th>Material</th>
<th>Surface Condition</th>
<th>Size (Normal Distribution p value)</th>
<th>DP Data (Normal Distribution p value)</th>
<th>Regression ((r^2 = m \cdot \text{size} + b)) ((r^2, p \text{ value}))</th>
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<td>0.198'0</td>
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APPENDIX B

Literature Review
<table>
<thead>
<tr>
<th>Author, Date and Journal</th>
<th>Experimental Conditions</th>
<th>Experimental Method</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlas, D. et al., 1982 Water Resource</td>
<td>- Amherst tap water - pH = 6.8 - air saturated, deaerated and air saturated chlorinated (2 mg/L as Cl) - duration - 24 hours - 40-50 mg copper tubing drillings in flasks containing 100 mL test solution - effect of DO was determined using pairs of identical solutions - one aerated with air and the other deaerated</td>
<td>- measured copper concentrations using atomic absorption - data was the mean of 2 (at least) replicated</td>
<td>- pH = 6, after 24 hours air saturated, 0.25 mg/L deaerated, 0.25 mg/L air saturated, with chlorine, approx. 0.85 mg/L - pH = 8, Chloride (ppm) Cu (mg/L) 10 1.5 7.5 1.0 5 0.5 0 0.25 pH = 5 10 7.0 7.5 5.5 5 2.75 2 1.5 1 1.0 0 1.0</td>
</tr>
<tr>
<td>Reiber, H.S. and M. Benjamin, 1990 Corrosion</td>
<td>- Seattle tap water, copper - T = 25 °C, D.O. = 10 mg/L, pH = 7.8 - duration - 96 hours - slow velocity = 1 ft/s</td>
<td>- weight loss - electrochemical polarization</td>
<td>- pits - 2 mm in diameter, depth &lt; 0.1 mm - weight loss - Fresh Aged mpy 0.8 0.46 S.D. (%) 25 15 (S.D. is the norm. S.D. of the mean) - uniform corrosion rate over surface</td>
</tr>
<tr>
<td>Ogino, K. et al., 1988 Corrosion</td>
<td>- 99.84% Cu in distilled water, HCl, KOH - pH range = 2 - 12 - amplitudes 35, 55, 75 μm</td>
<td>- weight loss measurements</td>
<td>- chem. balance - accuracy 0.01 mg - after 2 hours go from pH 2 - 12 weight loss 4.5 - 0.25 cumulative - no errors given</td>
</tr>
<tr>
<td>Pisigan, Jr., R.A. and J.E. Singley, 1987 Journal AWWA</td>
<td>- jar tests - solutions with various pH and alkalinity levels - adding bicarbonate, adjusting pH, add CO, and air, pH=7.8-8.0 - other basic and acidic solutions also used - T = 20 °C, under flow conditions - duration - 10-20 days (lab study) - 10-12 months (field) - D.W.</td>
<td>- weight loss measurements (corrosion rate)</td>
<td>- dissolved copper - pH = 7.4, alk. = 184, Cu = 0.45-1.0 mg/L and pH = 8.0, alk. = 205, Cu = 0.5-0.95 mg/L (after 15 days) under aerated, deaerated and chlorine conditions - no. of samples and errors are not specified</td>
</tr>
<tr>
<td>Author, Title, Date and Journal</td>
<td>Experimental Conditions</td>
<td>Experimental Method</td>
<td>Observations</td>
</tr>
<tr>
<td>--------------------------------</td>
<td>--------------------------</td>
<td>---------------------</td>
<td>--------------</td>
</tr>
</tbody>
</table>
| Rehring, J.P. and M. Edwards  
Copper Corrosion in Potable Water Systems:  
Impacts of Natural Organic Matter and Water  
Treatment Processes  
* more porous scale may allow a higher rate of  
soil - metal contact, tending to increase the  
corrosion rate | - drinking water (potable water)  
- filtered with 0.45 um pore size  
- pH = 6, 7.5, 9  
- flow rate = 0.5 gpm  
- T = 15°C  
- typical water pH levels = 6.4, 8.1 | - electrochemical testing - potentiostatic techniques - potentiodynamic  
- SEM | - NOM has an adverse effect on Cu corrosion rates at pH = 6 and lesser at higher pH  
- alum coagulation treated waters have higher corrosion rates than did those coagulated with  
ferric chloride  
- GAC adsorption increased corrosion rates,  
ozonation had little or no impact |
The pitting corrosion of copper  
Journal AWWA | - solutions prepared using deionized water and  
various salts and/or NOM (chloride exp)  
- (NaCl, NaSO4) | - electrochemical corrosion rate testing - Reiber cell | - literature review - theory of pitting  
corrosion rates profoundly impacted by the  
presence of NOM  
- chloride is more aggressive towards Cu (short  
term) but in long term, not well understood  
- chloride induces scale and passivates corrosion  
and pitting  
- corrosion rate assuming all Cu goes into soi'n  
1/4" diam, 1 hr = 12 mg/L  
1" diam, 1 hr = 4 mg/L, 4 hr = 16 mg/L  
corrosion rates for 3 model waters with and  
without 2 mg/L, NOM, pH = 8.8, 10 mg/L,  
alkalinity, 20 mg/L sulphate and chloride, 0.025  
mg/L NO3, 0.3 mg/L w/out NOM |
| Brock, A.J. and J.M. Popplewell, 1979  
Corrosion rate and metal release rate of copper  
base condenser tube alloys in fresh water  
Corrosion 79  
International Corrosion Forum Devoted  
Exclusively to the Protection and Performance of  
Materials | - Cu alloys - Cg, CuNi 90:10  
- SA = 100 cm²  
- New Haven potable water - pH = 6.9, chloride = 20 mg/L, dissolved solids = 79 mg/L  
- exposed to 900 ml test solution in glass beaker  
- 25°C  
- times 1 to 1000 hours | - wt. loss - films removed by dissolution in 10% HCl at 175 °F  
- test soi'n and film stripping soi'n were made  
up to 1 litre and analyzed using GFAAS - low  
concentration in stripping soi'n  
- for alloy CA142  
T = 1 hr, total wt. loss = 0.015 mg/cm2  
T = 100 hr, wt. loss = 0.01 mg/cm²  
T = 1000 hr, wt. loss = 0.09 mg/cm²  
Cu release from alloy 706 on 0.1 M NaCl soi'n,  
less than 10% of the metal loss goes into soi'n as  
soluble copper, majority going as Cu2O in the  
corrosion product | |
| Page, G.G., et al., 1974  
Mechanism of new type of copper corrosion  
in water  
Australian Corrosion Engineering  
Vol.18 (November/December) | - water composition: pH = 7.1 - 8.6, chloride = 9  
18 g/m² Cl, chlorine = 0.00 - 0.3 g/m² Cl  
- flow | - corrosion potential measurements  
- comparison decantation - raw water results  
- decantation results  
- 1 d up to 1 ppm  
- 25 - 30 d up to 1 ppm  
- chem main  
- 5 d up to 0.5 ppm  
- 30 d up to 4 ppm  
- cyclic voltametry | - survey of water taps - 45% of the 241 taps  
showed Cu in excess of 1.5 g/m² in first 650 mL  
of water drawn  
- 15% of taps gave Cu conc'n in excess of 10  
g/m³ mostly in services with high exit velocities  
or many bends causing excessive turbulence |
<table>
<thead>
<tr>
<th>Author, Title, Date and Journal</th>
<th>Experimental Conditions</th>
<th>Experimental Method</th>
<th>Observations</th>
</tr>
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<tbody>
<tr>
<td>Traverso, P. et al., 1994</td>
<td>- Cu-30Ni-2Fe-2Mn</td>
<td>- corrosion resistance - polarization and potential measurements</td>
<td>[O2]_n = 6.5 ppm</td>
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<tr>
<td>Effect of sulphides on corrosion of Cu-Ni-Fe-Mn alloy in sea water</td>
<td>- sulphide polluted and unpolluted natural sea water</td>
<td>- surface film characterization by chem. analysis and XPS</td>
<td>[sulphide]_n = 0.1, 0.8 ppm</td>
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<tr>
<td>British Corrosion Journal</td>
<td>- pH never below 8</td>
<td>- wt. loss increases, reaches max and then decreases</td>
<td>e.g. 15 d, wt. loss = 175 ug/cm²</td>
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<tr>
<td>Vol. 29, No. 2</td>
<td></td>
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<tr>
<td>Sedahmed, G.H. et al., 1994</td>
<td>- Cu in acidified FeCl₃, two phases</td>
<td>- analysis of Cu ions by iodometry (eliminates interference of iron ions with cupric determination)</td>
<td>- plot of ln(Cu/C) vs. time of corrosion - straight line - slope = MT coeff.</td>
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<td>Mass transfer controlled corrosion of pipelines under two phase (gas-liquid) flow</td>
<td>- recirc. batch tubular reactor</td>
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<tr>
<td>British Corrosion Journal</td>
<td>- variables - sořn and gas velocity</td>
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<tr>
<td>Vol. 29, No. 2</td>
<td>- MT coefficient</td>
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<td>- distilled water solutions</td>
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<td>- 25°C</td>
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<td>Adelejoo, S.B. and Y.Y. Duan, 1994</td>
<td>- influence of bicarbonate ions on stability of Cu oxides and pitting corrosion</td>
<td>- X-ray diffraction (XRD)</td>
<td>- wt. change %</td>
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<td>Corrosion resistance of Cu₂O and CuO on copper surfaces in aqueous media</td>
<td>- exposure sořns - HCO₃⁻, CO₃²⁻</td>
<td>- SEM</td>
<td>- dissolved Cu content (mg/L) analyzed using AAS (1.87 - 16.42 mg/L)</td>
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<tr>
<td>British Corrosion Journal</td>
<td>- pH = 5.88 - 8.69</td>
<td>- AAS</td>
<td>- higher pH, lower Cu content</td>
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<td>Vol. 29, No. 4</td>
<td>- done in glass beakers</td>
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<td>- highest Cu content 16.4 mg/L, had 18 mg/L of chloride ions present</td>
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<td>- 21°C</td>
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<td>- higher bicarbonate ions, less dissolved Cu</td>
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<td>Adelejoo, S.B. and Y.Y. Duan, 1994</td>
<td>- formation of cuprous and cupric oxides on metal surface</td>
<td>- wt. loss for NaCl and ammonia</td>
<td>- wt. loss given as a percentage with time</td>
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<tr>
<td>Influence of bicarbonate ions on stability of copper oxides and copper pitting corrosion</td>
<td>- immersion in acetate buffer or NaOH sořn</td>
<td>- polarization measurements</td>
<td>- Cu₂O occurs at pH&gt;4.8</td>
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<tr>
<td>British Corrosion Journal</td>
<td>- NaCl, ammonia, sodium bicarbonate</td>
<td>- XRD analysis</td>
<td>- CuO occurs at pH&lt;6.7</td>
</tr>
<tr>
<td>Vol. 29, No. 4</td>
<td></td>
<td></td>
<td>- potentiodynamic measurements of tap water, pH = 7.5, Cl = 23 0 mg/L</td>
</tr>
<tr>
<td>Mansfield, F. and Y. Wang, 1994</td>
<td>- Cu-Al alloys</td>
<td>- surface properties by EIS</td>
<td>- pH range 6.8 - 10.8</td>
</tr>
<tr>
<td>Corrosion protection of high copper aluminum alloys by surface modification</td>
<td>- immersion in boiling Ce(NO₃)₃</td>
<td>- impedance studies</td>
<td>- corrosion rate = 0.499-96 ug/m²/s</td>
</tr>
<tr>
<td>British Corrosion Journal</td>
<td>- anodic pol. in Na₂MoO₄ and immersion in boiling CeCl₃</td>
<td>- SEM</td>
<td></td>
</tr>
<tr>
<td>Vol. 29, No. 3</td>
<td>- immersion in 0.5M NaCl for 30d</td>
<td>- EDS for elemental mapping</td>
<td></td>
</tr>
<tr>
<td>Notoya, T., et al., 1995</td>
<td>- Ca, Mg, Na salt derivative of phytic acid</td>
<td>- wt. loss</td>
<td>- pH range 6.8 - 10.8</td>
</tr>
<tr>
<td>The corrosion and polarization behaviour of</td>
<td>- synthetic domestic water</td>
<td>- potentiodynamic and potentiostatic techniques (polarization meas.)</td>
<td>- corrosion rate = 0.499-96 ug/m²/s</td>
</tr>
<tr>
<td>copper in domestic water in the presence of Ca, Mg and Na-Salts of phytic acid</td>
<td>- pH = 6.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion Science</td>
<td>- 30°C, 65°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol. 37, No. 1</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Author, Title, Date and Journal</td>
<td>Experimental Conditions</td>
<td>Experimental Method</td>
<td>Observations</td>
</tr>
<tr>
<td>-------------------------------------------------------------------</td>
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<td>----------------------------------------------------------</td>
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</tr>
<tr>
<td>Mansfield, F., et al., 1994</td>
<td>- artificial sea water, natural</td>
<td>- polarization measurements under rotation</td>
<td>NS AS (µm yr⁻¹)</td>
</tr>
<tr>
<td>The corrosion behaviour of copper alloys, stainless steels and</td>
<td>- Cu, 90Cu:10Ni, 70Cu:30Ni, brass, Al-bronze, stainless steel, titanium</td>
<td>- instantaneous corrosion rates</td>
<td>Copper 7d</td>
</tr>
<tr>
<td>titanium in seawater</td>
<td></td>
<td>- wt loss of copper</td>
<td>65</td>
</tr>
<tr>
<td>Corrosion Science</td>
<td></td>
<td>- SEM, ESEM, EDS</td>
<td>90d</td>
</tr>
<tr>
<td>Vol.36, No 12</td>
<td></td>
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<td>20</td>
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<td>CuNi 90:10</td>
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<td>CuNi 70:30</td>
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<tr>
<td>Modestov, A.D., et. al., 1994</td>
<td>- copper in CI and benzotriazole containing acidic or neutral sol'ns</td>
<td>- voluntary, anametry, photocurrent response, impedance</td>
<td></td>
</tr>
<tr>
<td>A study of the electrochemical formation of Cu(1)-BTA films on</td>
<td></td>
<td>measurements</td>
<td></td>
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<tr>
<td>copper electrodes and the mechanism of copper corrosion inhibition in</td>
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<tr>
<td>aqueous chloride/benzotriazole solutions</td>
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<tr>
<td>Corrosion Science</td>
<td></td>
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<tr>
<td>Vol.36, No 11</td>
<td></td>
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<tr>
<td>Wang, Y.Z., et. al., 1994</td>
<td>- seawater</td>
<td>- electrochemical testing (polarization curves,</td>
<td></td>
</tr>
<tr>
<td>The effect of temperature on the corrosion behaviour of a 70/30</td>
<td>- various temperatures - 20, 40, 60 and 80°C</td>
<td>impedance)</td>
<td></td>
</tr>
<tr>
<td>Cu-Ni commercial</td>
<td>- pH = 8.2</td>
<td>- surface oxides analyzed by chemical and XPS methods</td>
<td></td>
</tr>
<tr>
<td>seawater</td>
<td>- DO = 6.5 - 3.0 ppm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Corrosion Science</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vol.36, No 8</td>
<td></td>
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<tr>
<td>Edwards, M., et al., 1994</td>
<td>- Cu pitting</td>
<td>- cyclic polarization expts</td>
<td></td>
</tr>
<tr>
<td>Inorganic anions and copper pitting</td>
<td>- oxygenated solutions containing bicarbonate,</td>
<td>- potentiostatic testing (electrochem. testing)</td>
<td></td>
</tr>
<tr>
<td>Corrosion</td>
<td>chloride, nitrate, perchlorate, sulphate ions</td>
<td>- SEM</td>
<td></td>
</tr>
<tr>
<td>Vol.50, No 5</td>
<td>- pH values - 5, 7, 9, 10, 10.0</td>
<td></td>
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<tr>
<td></td>
<td>- T = 8.5°C</td>
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<td>- anions added to deionized water</td>
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<tr>
<td>Author, Title, Date and Journal</td>
<td>Experimental Conditions</td>
<td>Experimental Method</td>
<td>Observations</td>
</tr>
<tr>
<td>-----------------------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------------------</td>
<td>-------------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Kato, C. et al., 1980</td>
<td>- Cu-9.4Ni-1.7Fe alloy (CDA706)</td>
<td>- wt. measurements - thickness was measured</td>
<td>- wt. loss with time</td>
</tr>
<tr>
<td>On the mechanism of corrosion of Cu-9.4Ni-1.7Fe</td>
<td>- aerated</td>
<td>- anodic and cathodic polarization curves</td>
<td>1 hr = 0.05 mg/cm²</td>
</tr>
<tr>
<td>alloy in air saturated aqueous NaCl solution</td>
<td>- 3.4 wt. % NaCl soln</td>
<td>- XPS, Auger electron spectroscopy and/or X-ray diffraction</td>
<td>1000 hr = 1.5 mg/cm²</td>
</tr>
<tr>
<td></td>
<td>- time up to 191 days</td>
<td></td>
<td>100 hr = 0.75 mg/cm²</td>
</tr>
<tr>
<td></td>
<td>- fresh and corroded samples</td>
<td></td>
<td>350 hr = 0.1 mg/cm²</td>
</tr>
<tr>
<td></td>
<td>- pH adjusted to 8</td>
<td></td>
<td>- wt. loss follows a parabolic rate law</td>
</tr>
<tr>
<td>Diem, C.B. and M.E. Orazem, 1994</td>
<td>- seawater (3.4% NaCl)</td>
<td>- electrochemical measurements</td>
<td>- velocity enhancement of the corrosion rate seen, other than that which could be accounted for by MT</td>
</tr>
<tr>
<td>Influence of velocity on corrosion of copper in</td>
<td>- flowing conditions</td>
<td>- scanning ellipsometer</td>
<td>- enhancement was actually less than that which would have been caused by increased overall MT</td>
</tr>
<tr>
<td>alkaline chloride solutions</td>
<td>- aerated</td>
<td>- measured film thickness</td>
<td></td>
</tr>
<tr>
<td>Corrosion, Vol. 50, no. 4</td>
<td>- pH = 8.5, 9.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>- T = 25°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Singh, M.M., et al., 1994</td>
<td>- copper</td>
<td>- wt. loss</td>
<td>- inhibitor efficiencies given for wt. losses - just a ratio of values with and without the inhibitor</td>
</tr>
<tr>
<td>Inhibition of copper corrosion in aqueous sodium</td>
<td>- 1.5% sodium chloride soln</td>
<td>- electrochemical experiments - un stirred and deacrated solns</td>
<td>- all inhibitors were effective in controlling the rate of Cu corrosion</td>
</tr>
<tr>
<td>chloride solution by various forms of the piperidine</td>
<td>- inhibitors - piperidine, piperidine dithiocarbamate and its Cu(II) complex</td>
<td></td>
<td></td>
</tr>
<tr>
<td>moiety Corrosion, Vol. 50, No. 8</td>
<td>- T = 25°C</td>
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</tr>
<tr>
<td></td>
<td>- solns prepared in doubly distilled water</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Edwards, M., et al., December 1994</td>
<td>- copper</td>
<td>- electrochemical analysis - potentiostatic measurements, polarization resistance measurements</td>
<td>- wt. loss data from previous research - at pH values of 8, alk = 1.3 mg/L</td>
</tr>
<tr>
<td>Effect of selected anions on copper corrosion rates</td>
<td>- simple solutions containing bicarbonate, chloride, perchlorate, nitrate, sulphate</td>
<td></td>
<td>T=100 days, wt. loss = 25 mg</td>
</tr>
<tr>
<td>Journal AWWA</td>
<td>- pH = 5.5, 7.0, 8.5, 10</td>
<td></td>
<td>T=200 days, wt. loss = 30 mg</td>
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<tr>
<td></td>
<td>- typical of drinking water</td>
<td></td>
<td>at pH values of 8, alk = 0.20 mg/L</td>
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<tr>
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<td>- made up with deionized water</td>
<td></td>
<td>T=100 days, wt. loss = 40 mg</td>
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<td>T=200 days, wt. loss = 65 mg</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Author, Date and Journal</th>
<th>Experimental Conditions</th>
<th>Experimental Method</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Ijsseling, F.P., et. al., 1982  
British Corrosion Journal | - sea water, copper  
- flow=1.5 m/s  
- rotational speed=1500 rpm  
- room temperature  
- well aerated  
- Vol:SA = 100:1 | - weight loss  
- free corrosion potential | - 47.9 d exposure, 10°C: 159.1 μm/y  
- 70 d exposure, 10°C: 55.6, 58.3 μm/y  
- average values 68.1 and 87.4 μm/y  
- 137.8 d, 20°C: 35.3 μm/y, 36.5 μm/y  
- 104.4 d, 10°C: 44.3 μm/y, 48.7 μm/y |
| Efird K.D. and D.B. Anderson, 1975  
Materials Performance | - sea water, Cu:Ni 90:10 and 70:30, (10*15*0.6)cm  
- duration - 14 years total  
- quiet sea water, flow (0.6 m/s) and tidal conditions | - specimens cleaned in 10% sulphuric acid, rinsed in distilled water and air dried  
- weight loss measurement  
- depth of localized attack | - 90:10:  
flow: 20-50 mg/cm²: 13-1 μm/y  
quiet: 5-10 mg/cm²: 4-1 μm/y  
- 70:30:  
flow: 20-53 mg/cm²  
quiet: 0.33 mg/cm² |
| Francis, R., 1985  
British Corrosion Journal | - sea water, Cu:Ni 90:10 and 70:30  
- T in heat transfer zone = 90±5°C  
- duration - 2 months  
- pH = 7.2-8.2  
- ammonia and chloride effects | - depth of impingement attack | - 90:10:  
0.03-0.09 mm (no iron), 0-0.02 mm (iron)  
- 70:30:  
0.10-0.16 mm (no iron), 0.01-0.21 mm (iron) |
British Corrosion Journal | - sea water, Cu:Ni 70:30  
- quiescent solutions  
- pH = 8.0, D.O. = 6.5 mg/L, T = 25°C  
- duration - 24-720 hours | - AAS - oxidized amounts of Cu and Ni in solution and corrosion layer  
- Polarization curves  
- X-ray diffraction | Time(hr) Solution Total Total Wt. Loss  
24 187 202 312  
360 1519 1625 2584  
720 1523 1717 2733  
(* all units are in μg/cm²) |
| Syrett, B.C. and Wing, S.S., 1980  
Corrosion | - aerated and deaerated sea water, Cu:Ni 90:10 and 70:30  
- recirculating flow loop, varying velocities  
- 2.54 cm lengths, 1.35 cm inside diameter  
- initial pH = 8.2, salinity = 29 ppt, T = 23.2±1.3°C, D.O. = 6.60 g/m³ | - weight loss  
- linear polarization  
- AC impedance and potential sweep | - air-saturated sea water:  
90:10, 0.5 m/s: 31.9 ± 1.1 mg  
5.0 m/s: 112.7 ± 22.1 mg  
70:30, 0.5 m/s: 19.9 ± 3.6 mg  
5.0 m/s: 20.6 ± 0.4 mg  
- deaerated sea water:  
90:10, 3 m/s: 6.66 ± 0.07 mg  
5 m/s: 34.3 ± 1.3 mg  
70:30, 3 m/s: 5.58 ± 0.44 mg  
5 m/s: 6.85 ± 0.85 mg |
<table>
<thead>
<tr>
<th>Author, Date and Journal</th>
<th>Experimental Conditions</th>
<th>Experimental Method</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mor, E. D. and A. -M. Beccaria, 1975 Corrosion</td>
<td>- sea water (deaerated and aerated), copper - 50 mm (length) by 7 mm (diam) - pH = 6.5-8.6, T = 25 °C - duration = 48 hours - 4 conditions: (1) aerated, sulphides (115 ppm), D.O. = 7.5 ppm, (2) aerated, no sulphides, D.O. = 7.5 ppm, (3) deaerated (D.O. &lt; 0.2 ppm), no sulphides, (4) deaerated (D.O. &lt; 0.2 ppm), various sulphides - continuous stirring, 200 rpm (disk)</td>
<td>- weight loss - X-ray diffraction - wt. loss calculated by adding the quantity of metal passing into solution to that adhering to the specimen (corrosion products) - Polarographic technique with superimposed sinusoidal voltage - Tacussel polarograph, PGR-3</td>
<td>pH Cu&lt;sub&gt;sea&lt;/sub&gt; Cu&lt;sub&gt;corr&lt;/sub&gt; Cu&lt;sub&gt;CD&lt;/sub&gt; 6.5 258-1120 470-955 10-60 7.2 50-1535 500-1250 10-22 7.9 88-1906 570-1470 10-15 8.6 54-2474 550-1730 15-54 (* all units are µg/cm²)</td>
</tr>
<tr>
<td>Lee, T.S., 1983 Corrosion</td>
<td>- sea water, Cu: Ni 90:10 (0.14<em>1.9</em>10) cm - T = 50 ± 5 °C for most tests, 23 ± 3 °C - velocity = 1.0 m/s (nominal) - copper release rate evaluation - 3 specimens exposed to 1 L of recirculating sea water, 1 cm², water exchanged every hour duration - 8 hours - copper release in 19 separate control tests</td>
<td>- concentrations analyzed using bicinchoninate - atomic absorption to determine accuracy of the above measurement - gravimetric analysis for weight loss - polarization curves - Auger electron spectroscopy analysis - composition of film</td>
<td>Rate of copper release for control spec's exposed to recirculating sea water at 50 °C Time (hours) Cu conc'n 1 0.15 6 0.5 12 1.15 24 2.25 (* units of mg/cm²) The mean rate after 8 hours was 0.09 ± 0.02 mg/cm² and in the final 2 hours 0.08 ± 0.03 mg/cm² (error is SD) Sea water at 25 °C, velocity 0 m/s: 3.7 mg/cm² (1.0 cm²)</td>
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<tr>
<td>Efed, K.D., 1977 Corrosion Journal</td>
<td>- clean, full strength sea water, copper based alloys (Cu: Ni 90:10, 70:30) - flow parallel to sample - pH = 8.0, T = 18 °C, Chloride = 19.0 g/L, D.O. = 6.4 ppm - duration - 30 days</td>
<td>- weight loss measurements (taken to 0.1 mg) - depth measurements</td>
<td>Weight loss measurements Weight (g) Flow (m/s) 0.5 1.5 0.75 3.0 1.0 6 1.25 7.5 1.6 15</td>
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<tr>
<td>Syrett, B.C and MacDonald, D.B., 1979 Corrosion</td>
<td>- recirculating sea water, tubular copper-nickel alloys - water velocity = 1.62 m/s - various oxygen levels - T = 26 ± 2 °C</td>
<td>- weight loss (2) - linear polarization (1) - AC-impedance (1) - potential step (1) (number of samples)</td>
<td>- comparison between measured and calculated weight loss DO(mg/dm²) Duration(h) Weight loss(mg) 0.045 336.5 5.92 ± 0.3 90-10 26.3 196 3.18 ± 0.1 90-10 0.045 336.5 1.65 ± 0.35 70-30 26.3 196 9.33 ± 0.03 70-30 0.045 0.42 ± 0.02 mg/day 90-10 0.045 0.12 ± 0.02 mg/day 70-30</td>
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<td>Experimental Method</td>
<td>Observations</td>
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<td>Beccaria, A.-M., et al., 1991 Corrosion Science</td>
<td>Cu:Ni 70:30 in polluted and unpolluted sea water (1.5<em>4.5</em>0.2)cm, T=25 °C, conditions - (1) aerated sea water, D.O. = 6.5 ppm, sulphide = 0, (2) aerated sea water, sulphide 2-10 ppm, (3) deaerated sea water, sulphide=0, D.O. &lt; 0.2 ppm, (4) deaerated sea water, 0 &lt; D.O. &lt; 0.2 ppm, 2 &lt; sulphide] &lt; 10 ppm, duration - 24, 68, 120, 240, and 384 hours in aerated solutions and 48 hours in deaerated</td>
<td>- weight loss (the amount of Cu and Ni combined as insoluble corrosion products adherent to corroded surfaces added to the amount of those two elements present in solution as soluble corrosion products) - Flameless and flame atomic absorption spectroscopy - ionic chromatography - gas chromatography - spectrophotometry - X-ray diffractometry</td>
<td>All at 0 sulphide concentration - aerated Cu wt. loss: 900 µg/cm² - deaerated Cu wt. loss: 300 µg/cm² - aerated Cu/Ni loss: 200 µg/cm² - deaerated Cu/Ni loss: 175 µg/cm²</td>
</tr>
<tr>
<td>Al-Hajji, J.N. and M.R. Reda, 1992 Corrosion Science</td>
<td>sea water (distilled water and standard sea water salt), Cu:Ni 90:10 and 70:30, sulphide introduced, experiments done repeatedly under the same environmental conditions to obtain reproducible results - unpolluted sea water reproducibility was good (deviation &lt; 5%), in polluted sea water (less than 10% margin of error)</td>
<td>- electrochemical corrosion measurements at 20 °C - potentiostat/galvanostat (EG&amp;G)</td>
<td>90:10 alloy - aerated and stirred, 0 ppm sulphide, 2.65 - 2.69 mpy - aerated and stagnant, 0 ppm sulphide, 0.695 mpy 70:30 alloy - aerated and stirred, 0 ppm sulphide, 1.16 mpy - aerated and stagnant, 0 ppm sulphide, 0.09 mpy</td>
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<td>Experimental Conditions</td>
<td>Experimental Method</td>
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| Tamba, A., 1982 British Corrosion Journal | - NaCl solution (35 g/L), Cu:Ni 90:10  
- tubing 1.0 mm  
- flow: 2.0 m/s  
- T = 50 °C  
- aerated  
- duration: 60 days | ATEL CS 100/3 corrosion meter (mm/y) | - 1.2 mm/y to 0.05 mm/y after 60 days  
- 0 to approximately 8 mg/cm² after 60 days |
| Mor, E.D. and Beccaria, A.-M., 1978 British Corrosion Journal | - 3.5% NaCl solution and sea water, soft copper 99.8% (40*8*1) mm  
- pH = 7.8, D.O. = 7 ppm  
- stainless steel vessel with teflon lining  
- varying pressures | weight loss calculated by addition of the amount of copper determined in solution to the amount of copper still remaining in the form of corrosion products  
- potentiostatic tech and superimposed sinusoidal alternating current  
- X-ray diffractometry (corr. products) | - time 0 to 360 hours, in 3.5% NaCl: 0 to 1000 µg/cm² and in sea water: 0 to 750 µg/cm² (both at 1 atm pressure) |
- pH=5, T=25 °C, D.O. = 8 ppm  
- flow velocity = 0.45 m/s  
- five specimens (all expected to be consistent) | direct weight loss measurement (1)  
- small amplitude cyclic voltammetry (SACV) (2)  
- electrochemical impedance spectroscopy (EIS) (1)  
- potentiodynamic polarization measurements (1) | Flow through pipe:  
Velocity(m/s) Duration(h) Weight loss(mg)  
0.31 94 0.043  
4.37 150 2.047  
(measured weight losses) |
| Hulquist, G. et. al., 1987 Corrosion Science | - pure copper in neutral solutions (distilled water and 0.5 M NaCl) and acid solutions (1 M and 9.2 M HNO₃ and H₂SO₄)  
- specimens (15*12*2) mm, polished  
- for gamma-specroscopy measurements, specimens (30*30*0.4) mm  
- available amount of solution > 2 mL cm²/h | weight loss measurements  
- gamma spectroscopy for solution analysis  
- electron spectroscopy for chemical analysis (ESCA) for surface characteristics | dissolution rates approximated to corrosion rates because the growth of reaction products on the copper was negligibly small relative to the metal species found in the solution at these conditions of immersing  
- stirring solution  

\[
\text{[Cu] } \mu g/cm²/h \\
\begin{align*}
\text{distilled water} & : 0.6 \quad \text{- gamma spec} \\
0.5 \text{ M NaCl} & : 0.9 \quad \text{- gamma spec} \\
1.0 \text{ M HNO}_3 & : 7 \times 10^7 \quad \text{- wt. loss} \\
9.2 \text{ M HNO}_3 & : 2 \times 10^7 \quad \text{- wt. loss}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Author, Date and Journal</th>
<th>Experimental Conditions</th>
<th>Experimental Method</th>
<th>Observations</th>
</tr>
</thead>
</table>
| Reiber, S.H., et al., 1987 Journal AWWA | - Seattle tap water, copper pipes  
- pH = 5.7-6.2, 7.8-8.3  
- free chlorine = 0.2 mg/L  
- duration = 500 hours  
- low mineral content  
- added lime, soda ash | - weight loss measurement  
- linear polarization | - weight loss from the pipes was reduced from 21.6 mg/L down to 10.2 mg/L through water treatment  
- inaccuracies and variabilities associated with each method  
- not given variability, just regressions not probabilities associated with the result |
| Stone, A. et al., 1987 Journal AWWA | - Seattle tap water, copper pipes  
- pH = 6.5-7.0  
- Cl = 0 mg/L  
- flow rate = 5.6 cm/s  
- added sodium sulphate to the water  
- low mineral content | - weight loss measurement  
- linear polarization | Results  
- 1.14 ± 0.17 μm/y (15 percent)  
- 0.67 ± 0.13 μm/y (19 percent)  
- 0.33 ± 0.05 μm/y (15 percent)  
- error is quite high resulting from weight loss measurements, replicates |
- pH = 7.3-9.4, Cl = 3 - 1032 mg/L  
- water flow/stagnation  
- tap water or deionized water (lab study) | - concentration measurement  
- (analytical technique not presented) | - highest copper concentration = 1 mg Cu/L (standing and running)  
- concentration given for up to 168 days |
- pH = 6-6.5 (alkalized to a pH of 9-9.5)  
- added chlorine = 11 mg/L  
- D.O. = 0.9 mg/L  
- duration - 310 days | - concentration measurements of total tube volume  
- SEM/EDAX  
- pitting depth measurement | - 149 mg/L and 56 mg/L (not told how this was done nor how many samples were required, just two locations)  
- pit depth 90 μm to 110 μm after 310 days |
| Eriksen, T.E., et al., 1989 Corrosion Science | - copper foil in pure oxygen free water (deionized, double distilled water)  
- < 1 ppm D.O.  
- duration - 61 days | - atomic absorption spectrophotometry  
- ESCA  
- cathodic reduction | - corrosion products - dissolved from the copper surface  
Cu mg/dm²  
Cu 99.7% 21.5, 19.6, 21.5  
11.4, 15.0, 9.0  
Cu 99.9995% 30, 40, 25  
Corrosion rate calculated from dissolution of corr. prods.  
Cu Corr rate (μg/cm²/h)  
99.7 0.014, 0.0062  
99.995 0.021  
no. of samples not given, error not given |
<table>
<thead>
<tr>
<th>Author, Date and Journal</th>
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<th>Observations</th>
</tr>
</thead>
</table>
| Al-Hajjar, F.H. and F.M. Al-Kharafi, 1988 Corrosion Science | - deaerated tap water, copper  
- pH = 5.9, 7 and 9, T = 50 ± 1 °C  
- corrosion inhibitors present - ATZ and ADMP  
- chlorine level not given, sulphates = 80 ppm | - XPS studies | - calculated a corrosion rate (MMPY)  
Results after 4 hours immersion:  
pH = 5.5 - 0.04 mm/y (no inhibitor added)  
pH = 7 - 0.01 mm/y (no inhibitor added)  
pH = 9 - 0.02 mm/y (no inhibitor added)  
- no. of samples and error not given |
| Syrett, B.C., 1977 Corrosion | - pure water, OFHC copper (2.22 cm diam. by 2.54 cm length)  
- T = 30 ± 5 °C  
- flow = 10 ft/s (3.048 m/s) | - descaled weight loss  
(oxides dissolved in 10% vol. sulphuric acid and sulphides dissolved in 1.5 wt% potassium cyanide) | Results - time varied with speed  
Ws.loss O₂ ppb Time(min) Corr. rate  
0.8 6950 4440 < 0.4  
0.67 880 2585 < 0.4  
0.12 870 2720 4.1  
0.08 865 2728 6.74  
1.14 875 2695 12.2  
0.86 60 2995 1.0  
0.67 50 2725 0.4  
0.51 29 5425 NA  
(1 test specimen per test) |
- treatment chemicals and contaminants  
(amines, oxygen and carbon dioxide added)  
- pH = 6.6-9.0, T = 103-154 °C  
- flow rate = 200-1890 mL/min | - concentration measurement (plot concentration versus time)  
- acid injection | Concentration results  
- time = 0, [Cu] = 110 ppb, pH = 1.75  
- time = 3, [Cu] = 50 ppb, pH = 7.0  
(D.O. = 50 ppb, ammonia = 1.0 ppm, 154 °C, total flow rate = 1890 mL/min, nitric acid flow rate = 1 mL/min) (56 runs) |
- pH = 5.5-6.0  
- closed plastic container | - weight loss from concentration  
- concentration measurements - measure copper ions using a modified bathocuproine spectrophotometric method | - 0.7 ± 0.1 mm/h, solute effects  
- 6.0 ± 1 mg/m² h  
- [Cu] range = 0.180 - 0.515 mg/L  
- using teflon, not accounting for adsorption  
- testing done in duplicate (or triplicate), accompanied by blanks (subtracted from results) |
| Knutsson, L. et al., 1972 British Corrosion Journal | - aerated water (tap water)  
- pH = 6.5, 8, T = 30 °C, 65 °C and 90 °C  
- flow rates = 3 m/s, 6 m/s  
- chloride = 5.0 to 7.0 mg/L  
- duration - 12 months | - depth of attack, μm | - no attack  
- < 30 μm  
- 70 μm  
(depending on flow rate)  
- no. of samples and error not given |
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| Moliere, M. et. al., 1990 Corrosion Science | - pickled copper in aerated deionized water  
- pH = 7.0, T = 70 °C, D.O. = 2-3 mg/L  
- duration - 24 - 72 hours, 200 hours  
- flow rate = 1.1 m/s | - measured the quantity of copper oxides collected on filters  
- X-ray analysis | - 5-10 mg/m² day  
May lose some of the product, not capturing all of the losses |
| Cohen, A., 1993 Materials Performance | - copper in potable water  
- flow rate = 0.25 l/min  
- water treatment techniques | - concentration measurements (do not specify which analytical technique was used) | - shows concentration versus pH level (pH = 8, [Cu] = 0.25 ppm)  
Not much confidence associated with this method |
- pH = 7.3-8.4, Cl⁻ = 16-45 mg/L, T = 13 °C  
- soda ash treatment | - examination for pitting attack  
- scanning electron microscopy  
- microchemical analysis and EDS  
- does not quantify the amount of copper lost to solution | - presence of pitting  
- oxidation products  
- non-aggressive pH of 8.1 to 8.3  
- 100 tube specimens, 50 for no treatment and 50 for soda ash treatment |
| Cornwell, F.J., et. al., 1973 British Corrosion Journal | - domestic water supplies  
- pH = 7.4, 7.5, 8.5  
- Cl⁻ = 48.5, 41.8, 29.0 ppm  
- low free chlorine values | - potential measurements  
- potential versus time curves  
- eddy-current examination | - potential changes with time, indicating pitting tendencies  
- used 12 uncleaneed tubes, 12 tubes abrassively cleaned with iron grit and 23 tubes cleaned with iron for 0.5 seconds or alumina grit for 5 to 30 seconds |
| Katakura, K. et. al., 1988 Corrosion Engineering (Tokyo) | - tap water with various amounts of chlorine  
- pH = 7.3, T = 60 °C  
- Cl⁻ = 31 mg/L, add NaClO, adjust pH to 7  
- copper pipe: O.D. = 12.76 mm, wall thickness = 0.64 mm, cut into 500 mm lengths  
- duration = 509, 531 and 659 days  
- flow rate = 0.3 m/s | - corrosion potentials  
- surface films and corrosion products were removed ultrasonically in dilute sulphuric acid  
- pit depths examined | - gives water composition but does not tell how it was analyzed  
- pit depth versus probability  
- highest pit depth = 0.46 mm, t = 599 days  
- 0.6 mm pit depth, t = 657 days  
- untreated, 10 mg/L, pit depth = 0.85 mm |
| Alam, I.A. and M. Sadiq, 1989 Environmental Pollution | - 150 drinking water samples collected - made up of desalinated sea water or groundwater, water chlorinated, pH adjusted (soda ash)  
- pH = 8.07 - 6.98, Cl⁻ > 400 mg/L other parameters not specified  
- under flow conditions | - ICP - argon analyzer  
- measurements repeated 5 times, determined the mean and standard deviations | - copper concentration ranged from 0 to 6.83 μg/L |
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<tbody>
<tr>
<td>Blum, W.J., et. al., 1994 Proceedings from the Fourth International Zebra Mussel Conference, Madison, Wisconsin</td>
<td>- electrolytic dissolution of copper into raw lake water (fresh water)</td>
<td>- graphite furnace atomic absorption spectrometry</td>
<td>- 10 ppb copper concentration will work (60% reduction in attachment) - conducting experiments in &quot;bio-boxes&quot; which are constructed from plexiglass which has been shown to adsorb copper from the solution resulting in a lower copper reading</td>
</tr>
<tr>
<td>Race, T.D., and M.A. Kelly, 1994 Proceedings from the Fourth International Zebra Mussel Conference, Madison, Wisconsin</td>
<td>- copper in lake water - water parameters are not specified - metal ion release rates - duration - two years - tests conducted in a polyethylene vessel</td>
<td>- Neutron Activation</td>
<td>- 1 - 2 mg Cu/cm² day release rate - do not account for losses to the walls of the vessel - Neutron Activation was not the most appropriate analytical technique for this work</td>
</tr>
<tr>
<td>Masson, D., 1994 Proceedings from the Fourth International Zebra Mussel Conference, Madison, Wisconsin</td>
<td>- copper corrosion in Lake St. Clair source water - pH = 5 and 8 - tests conducted in a glass vessel</td>
<td>- using procedure NSF 61 and analytical method EPA 220.2</td>
<td>- corrosion rates - do not account for adsorption to glass vessel walls</td>
</tr>
<tr>
<td>Brock, et. al., 1979 Paper presented at the International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, Atlanta, Ga.</td>
<td>- four copper alloys used - including Cu:Ni 90:10, in tap water - glass beaker, glass hooks - aerated solution, T = 40 °C - duration - 1-1000 hours</td>
<td>- weight loss - concentration measurements (test solutions and film stripping solutions analyzed</td>
<td>- after 1000 hours - approx. 0.12 mg/cm² (wt. loss) - corrosion rate 1 hr - 1 mpy 1000 h - 0.015 mpy - copper ion release - 0.11 mpy after 1 hour and 0.001 mpy after 1000 hr</td>
</tr>
<tr>
<td>Kodama, T., 1982 Proceedings of the International Symposium on Corrosion of Copper and Copper Alloys in Building</td>
<td>- copper tubes at a water treatment plant - pH = 6.4-7.4 - freshwater (Japanese) - low hardness, low carbonate, alkalinity, rel. low pH, high sulphide and silica - low buffer</td>
<td></td>
<td>- pH = 6.4, 12 mdd - pH = 7.2, approx. 2 mdd</td>
</tr>
<tr>
<td>Hilburn, R.D., 1983 Journal AWWA</td>
<td>- Seattle tap water, Cu plumbing - low salinity, low pH, low conductivity - pH = 6.0-6.3, Cl⁻ = 1.8-2.6 ppm - T = 5, 15, and 25 °C - duration - 4 months</td>
<td>- weight loss - electrochemical reactions - converted electrochemical measurements to weight loss - three point method by Barnatt</td>
<td>- standing river water, T=25°C, pH = 6.3, corr. rate = 0.23 mils/y - given various corr rates for the different reaction controlled events - pH=8.0, corr rate = 0.1 mpy, 0.25 mpy and 0.275 mpy</td>
</tr>
<tr>
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<td>Observations</td>
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<tr>
<td>Trewick, G.P., et. al., 1985 Journal AWWA</td>
<td>last water analysis, 1981 - pH = 6.9, chlorine = 0.3 mg/L, D.O. = 10-14 mg/L, chlorine residual = 1 mg/L - domestic/consumer distribution lines - chloramines versus free chlorine - duration - 16 months - flow rate = 2 fps, 7 flow paths</td>
<td>- drying, removing epoxy coating; mech. and chem. cleaning and weighing - copper and lead - samples analyzed - analytical method not specified</td>
<td>- corrosion rates under free chlorine levels after 3 months = 1.5-3.25 mg/dm³/day and after 18 months = 1.75 mg/dm³/day - steady state corr and penetration rates of 1.7 mg/dm³/day, 0.3 mils/yr</td>
</tr>
<tr>
<td>Gilbert, P.T., 1966 Proceedings of the Society of Water Treatment Examination</td>
<td>cuprosolvent waters - pH levels = 4.9-6.9, chloride=8-84 ppm - pH = 5.6-7.7, Cl⁻ = 11-26 ppm, oxygen no given</td>
<td>- weight loss - pit depth - dimensional change</td>
<td>- copper concentration levels given but the analytical method is not specified</td>
</tr>
<tr>
<td>Hummer, 1968 Materials Protection</td>
<td>- potable water - 60, 110 ppm hardness, pH levels not given - under flow conditions - duration - 16 years - varying temperatures</td>
<td>- gravimetric, micrometric and radiographic measurements</td>
<td>- max. loss of wall thickness: various diameters and speed of flow 50 °F = 2.5 mils loss, 3/8&quot; diam, 13.1 fps, 200°F, 18 mils 50 °F = 5 mils, 1.25 &quot; diam, 1.5 fps, 200 °F = 14 mils - changes with zeolite softening</td>
</tr>
<tr>
<td>Obrecht, M.F. and L.L. Quill, 1960 Heating, Piping and Air Conditioning</td>
<td>- plumbing systems - tap water with copper electrode - 10 s cathodic current pulse of 0.01 mA then 10 s of 0.01 mA anodic current then 10 s 0.01 mA cathodic current etc. - 20 consecutive cycles - pH = 7.5, 8.64, Cl⁻ = 18.4 ppm, 29 ppm</td>
<td>- dissolved copper 8 day test by ICP every 30 hours</td>
<td>- tap water (loss in mg Cu/cm³)</td>
</tr>
<tr>
<td>Akkaya, M. and J.R. Aubrose, 1987 Corrosion</td>
<td>- copper in potable water, un stirred at room temperature - specimens suspended in capped quart jars filled with relatively soft, quiescent reservoir water, changed every 6 weeks - pH = 6.5-7.5, Cu = 0.01-0.1 mg/L, Cl⁻ = 4-7 mg/L, D.O. = 13.7-14.3 mg/L - duration - 13 years</td>
<td>- corrosion products were removed by a suitable acid or by scrubbing with detergent or both, using ultrasonic cleaning where necessary - max. pit depths determined microscopically or by a depth gauge - values converted to mils per year</td>
<td>- copper (99.9%) - average penetration 0.017 mils/y - Cu:NI (90:10) - 15 yrs, 0.011 mils/y</td>
</tr>
</tbody>
</table>
APPENDIX C

X-ray Photoelectron Spectrometry Analytical Method

(from Dr. T. Debies, Xerox, Webster, New York)

The electron spectra of carriers were measured with a Kratos XSAM 800 Electron Spectrometer. The base pressure of the instrument is typically in the $1 \times 10^{-7}$ Pa range. The sections were irradiated with Al $k\alpha$ X-rays at a power of 300 Watts (15 kV, 20 mA). The spectrometer was calibrated with reference to the Au $4f_{7/2}$ line at 84.0 eV and the Cu $2p_{3/2}$ line at 932.6 eV. Using these references the binding energy of the C $1s$ hydrocarbon line for hydrocarbon contamination on a gold substrate is 284.8 eV.

The sections are presented to the X-ray beam by mounting them on a stainless steel stub. Sections are prepared by flattening the tube sections between two clean stainless steel plates. This removes the curvature of the tubing and permits acquisition of spectra at a higher signal to noise ratio than possible for a curved sample. The tube sections are held to the stainless steel stub with an adhesive and silver paste. The silver paste also helps make good electrical contact between the sample and the spectrometer. The stubs are placed on the sample carrousel holder and introduced into the spectrometer's vacuum sample treatment chamber for pumpdown prior to introduction into the main analytical chamber. Typical introduction times to ultra-high vacuum are one half hour.

Initially, an elemental survey scan from 0 eV binding energy to 1000 eV binding energy is obtained to identify all elements present on the surface. After identification of the elements, medium energy resolution spectra are acquired for the principal line of each identified element. The spectrometer is operated in the Fixed Analyzer Transmission mode at a pass energy of 20 eV. This permits spectra to be acquired rapidly due to the enhanced sensitivity at this pass energy, but still
allows sufficient energy resolution to identify chemical states. Good signal to noise ratios are important for reproducible quantitative analyses.

The number of scans for each element is dependent upon the strength of the signal for the principal line. Typically the scan length for a single scan of the principal line of each element is 60 seconds. Data points are acquired at every 0.1 eV. For carbon, copper, and oxygen at least 10 scans are acquired and time averaged. Weaker signals for silicon, nickel, calcium, and nitrogen require approximately 20 to 25 scans per element at 60 seconds per scan.

Quantitative analyses employ the empirical sensitivity factor method for peak areas, not peak heights. In this method the peak area of the principal line of each element is determined using computer software. The peak area is divided by an empirical sensitivity factor for the specific element. The "adjusted" peak area for an element is then divided by the sum of the "adjusted" peak areas for all of the elements in the sample. The result is the concentration for that element in units of atomic percent. Using the atomic mass, the atomic percent can be converted to a weight percent. Both values are reported to the customer. The empirical sensitivity factors are instrument and matrix dependent. The empirical sensitivity factors are relative and based on a literature value of F 1s = 1.00. We used kynar for a carbon standard that incorporated both carbon and fluorine. From the empirical formula for kynar and assuming a sensitivity factor of F 1s = 1.00, we determined the sensitivity factor for the C 1s line. Once the sensitivity factor for carbon was determined we analyzed PMMA and determined the sensitivity factor for O 1s. Once the factors were determined for C 1s and O 1s we analyzed nylon 6,6 and determined the sensitivity factor for N 1s. The factors used for carriers are summarized in the table below. The sensitivity factors for Cu, Zn, and Ni were determined from the metal fluorides.


<table>
<thead>
<tr>
<th>Elemental Line</th>
<th>Sensitivity Factor</th>
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</thead>
<tbody>
<tr>
<td>F 1s</td>
<td>1.00</td>
</tr>
<tr>
<td>C 1s</td>
<td>0.200</td>
</tr>
<tr>
<td>N 1s</td>
<td>0.280</td>
</tr>
<tr>
<td>O 1s</td>
<td>0.560</td>
</tr>
<tr>
<td>Cu 2p_{3/2}</td>
<td>2.75</td>
</tr>
<tr>
<td>Ni 2p_{3/2}</td>
<td>2.55</td>
</tr>
<tr>
<td>Zn 2p_{3/2}</td>
<td>4.00</td>
</tr>
</tbody>
</table>

Using this method, precisions of better than 5% relative can be achieved for the major constituents, 10% relative for minor constituents and 20% relative for elements present at concentrations of less than 1 atomic percent. Precision gains through increasing the scan times are achieved at the rate of the square root of the time and are not directly proportional to the increase in time. Doubling the precision for a constituent requires a four fold increase in scan time.

The limits of detection for the technique are approximately 0.1 atomic percent for carriers. The limits of detection can be extended to approximately 0.03 atomic percent or better if the analyst has prior knowledge to the presence of an element from a more sensitive technique. Scan times can be extended and energy resolution decreased to increase sensitivity.