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UTILIZATION OF COPPER ALLOYS FOR MARINE APPLICATIONS

BY

ANDREW DRACH
B.S. in Mechanical Engineering, Kyiv Polytechnic Institute, Ukraine, 2008

DISSERTATION

Submitted to the University of New Hampshire
in Partial Fulfillment of
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in
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Dedicated to my Teachers
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Abstract

Utilization of Copper Alloys for Marine Applications

by

Andrew Drach
University of New Hampshire, May 2013

Utilization of copper alloy components in systems deployed in marine environment presents potential improvements by reducing maintenance costs, prolonging service life, and increasing reliability. However, integration of these materials faces technological challenges, which are discussed and addressed in this work, including characterization of material performance in seawater environment, hydrodynamics of copper alloy components, and design procedures for systems with copper alloys.

To characterize the hydrodynamic behavior of copper alloy nets, mesh geometry of the major types of copper nets currently used in the marine aquaculture are analyzed and formulae for the solidity and strand length are proposed. Experimental studies of drag forces on copper alloy net panels are described. Based on these studies, empirical values for normal drag coefficients are proposed for various types of copper netting. These findings are compared to the previously published data on polymer nets. It is shown that copper nets exhibit significantly lower resistance to normal currents, which corresponds to lower values of normal drag coefficient.

The seawater performance (corrosion and biofouling) of copper alloys is studied through the field trials of tensioned and untensioned specimens in a one-year deployment in the North Atlantic Ocean. The corrosion behavior is characterized by weight loss, optical microscopy, and SEM/EDX analyses. The biofouling performance is quantified in terms of the biomass accumulation. To estimate the effects of stray electrical currents on the seawater
corrosion measurements, a low cost three-axis stray electric current monitoring device is designed and tested both in the lab and in the 30-day field deployment. The system consists of a remotely operated PC with a set of pseudo-electrodes and a digital compass. The collected data is processed to determine magnitudes of AC and DC components of electric field and dominant AC frequencies.

Mechanical behavior of copper alloys is investigated through a series of uniaxial tension tests on virgin and weathered (after one-year deployment in the ocean) specimens. The changes in mechanical properties are quantified in terms of differences in Young's modulus, Poisson's ratio, ultimate strength, and ultimate strain. The obtained stress-strain data is used for numerical modeling of the mechanical behavior of chain-link nets. The simulations are compared with the experimental data on stiffness and strength of the nets.

The available information on seawater performance of copper alloys (corrosion, biofouling, mechanics) and copper alloy nets (hydrodynamics) is used to develop engineering procedures for marine aquaculture fish cage systems with copper alloy netting. The design, analysis, and fabrication procedures are illustrated on a commercial size gravity-type offshore fish cage deployed in the Pacific Ocean near Isla Italia (Patagonia, Chile).

The funding for this work was provided by the International Copper Association. This work was also supported through two UNH Fellowships: CEPS UNH Graduate Fellowship to Outstanding PhD Program Applicants and Dissertation Year Fellowship.
Chapter 1. Introduction

Design and analysis of structures for marine applications – such as traditional (oil and gas) and renewable (wind and tidal turbines) offshore energy installations, aquaculture, shipbuilding, and harbor protection – faces several technological challenges including material deterioration and biological fouling concerns (WHEA, 1984; Scott and Muir, 2000). Historically, timber, steel, and more recently polymers have been the primary materials used in marine applications due to their high availability, low cost and ease of manufacturing. However, these materials have limited service life and require regular maintenance due to high rates of deterioration and low fouling resistance in seawater (Moffatt & Nichol Engineers, 1983).

Development and utilization of copper alloy components for marine applications is being actively promoted by the industry due to their reduced maintenance costs, prolonged service life, increased reliability and high recyclability (Hunt and Bellware, 1967; Todd, 1991; Peters, 1991). However, introduction of these materials requires revision of established design techniques and analysis procedures due to the difference in material properties and manufacturing methods. The focus of this dissertation is on providing scientific solutions to the technological issues of transition to high performance copper alloys in marine applications. In particular, the following studies are included in this manuscript:

- Investigation of the hydrodynamic performance of copper alloy nets;
- Evaluation of corrosion and biofouling resistance of copper alloys in seawater through field trials in North Atlantic;
- Experimental studies of mechanical properties of copper alloys;
- Development of numerical modeling techniques to predict mechanical response of copper alloy structures in the marine environment;
• Development of the engineering procedures for design of marine aquaculture installations with copper alloy nets.

One of the areas where the usage of copper alloys can revolutionize the industry is marine aquaculture (Huguenin and Ansuini, 1975; Powell, 1976; Powell and Stillman, 2009). Marine aquaculture is a type of fish farming process, which takes places in rigid or flexible enclosures (usually fish nets) deployed in seawater environment (inshore and offshore). This is a rapidly growing industry with potential to satisfy the global seafood demand in the environment of declining wild fish harvesting (Naylor et al., 2009). Existing technologies rely on polymer netting, which experiences extensive biofouling (growth of microorganisms on the net which results in reduced supply of oxygen for fish) and does not provide proper protection from sea predators (sharks, seals, sea lions, etc.). In contrast, copper alloy nets have natural resistance to corrosion and biofouling combined with high strength and stiffness. In preliminary trials, copper netting exhibited excellent performance (WHEA, 1984; DeCew et al., 2010a; Chambers et al., 2010), but its hydrodynamic characteristics (forces exerted by waves and currents) are not presently known. To address this issue, experimental studies of the hydrodynamic response of copper alloy net panels were performed in the tow tank. The results of this testing are discussed in Chapter 2.

Service life and maintenance schedule of structures in marine environment are usually governed by the material corrosion and biofouling rates, and thus information on these parameters is important for design of systems for seawater deployment, especially in remote or deep locations. A one-year field deployment aimed to evaluate performance of eleven copper alloys in the marine environment was conducted over the period of August 2010 – September 2011. Data on the biofouling and material loss quantities was collected at 3-month intervals including visual observations (by means of digital imaging) and measurements of changes in weight and dimensions. The results of this testing are discussed in Chapter 3. To quantify the effect of electrical stray currents in the deployment location on the observed seasonal variations in corrosion rates, an electronic device was designed and deployed. The design and deployment of the electrical stray current monitoring device and the collected data are discussed in Chapter 4.
To effectively design structures with copper alloy components (in particular, with copper alloys nets), it is important to understand their structural response to the service loads in marine environment. The structural response is highly dependent on the following mechanical properties that are established in this work: stiffness, strength, and yielding behavior. Uniaxial tension tests were performed on plate and wire specimens to establish elastic tensile properties and ultimate strength of the alloys, following relevant ASTM standards. Additional tests were performed on the copper alloy net panels and netting connectors to determine the structural response and failure modes of these components. The results were compared against numerical simulations with the material properties collected from experiments, as discussed in Chapter 5.

Engineering approach to the design of structures with copper components for marine applications is significantly different from the methodologies developed for the systems with steel, polymer or wood components. My research provides engineering methodology for design and analysis of systems which can withstand regular service loads and survive through storms without substantial damage. To assist with smooth integration of copper nets into the existing aquaculture infrastructure, the procedures for construction, deployment, and recovery are developed in Chapter 6. The work on methodology development has been completed and tested on marine aquaculture systems deployed in the North Atlantic (DeCew et al., 2009) and South Pacific (Celikkol et al., 2010).
Chapter 2. Characterization of Geometry and Normal Drag Coefficients of Copper Nets

In this chapter, mesh geometry of the major types of copper nets currently used in the marine aquaculture is analyzed, and formulae for the solidity and strand length are given. Experimental studies of drag forces on copper alloy net panels are discussed. Based on these studies, empirical values for normal drag coefficients are proposed for various types of copper netting. These findings are compared to the previously published data on standard nylon nets. It is shown that copper nets exhibit significantly lower resistance to normal currents, which corresponds to lower values of normal drag coefficient.

2.1. Copper alloy nets in marine aquaculture

Marine aquaculture is a process of raising fish in fishcages that are located in the seawater environment. These cages consist of net chambers supported by rigid or flexible framework. Traditionally, nets are comprised of nylon netting, however, potential improvements in fish farming operations and maintenance can be achieved by substituting polymer nets with the copper alloy netting. In particular, copper nets show excellent resistance to corrosion and bio-fouling (Efird, 1975; Efird and Anderson, 1975; Powell and Stillman, 2009), good potential to protect fish against predator attacks (Huguenin and Ansuini, 1975), and increased structural integrity and stability of the net structure volume under extreme weather conditions. The effectiveness of the biofouling resistance of copper netting is illustrated in Fig. 2.1. A small volume cage with copper alloy netting was deployed for seven months at the Atlantic Marine Aquaculture Offshore Site operated by the University of New Hampshire (UNH). The photographs show heavy in-situ marine growth (Fig. 2.1a) on nylon portions of the net chamber (required for diver access and safety), while the copper alloy net is free of biofouling. This can be seen more clearly in (Fig. 2.1b) which shows a nylon net “diver access panel” adjacent to the copper mesh.

However, usage of copper alloy netting in marine aquaculture requires systematic studies and better understanding of the hydrodynamic performance of these components.
In this chapter, hydrodynamic drag of copper nets of various configurations and solidities is investigated and compared with experimental data and analytical predictions for nylon nets. Geometry, structure and alloy composition of copper netting made by various manufacturers are presented in Section 2.2. Analytical models to predict normal drag on net panels are reviewed in Section 2.3. Description of an experimental setup for investigation of drag on copper alloy nets is given in Section 2.4. Finally, in Section 2.5, the results of tow tests are compared to analytical models, and drag coefficients for copper net panels are proposed. Note that in the text to follow we refer to copper alloy nets of various types simply as "copper nets".

![Fig. 2.1. Photographs of a fishcage after seven month of deployment in the North Atlantic. Image of copper netting in the ocean with a section of biofouled nylon netting is shown in (a), heavily fouled diver door made of nylon is depicted in (b).](image)

### 2.2. Geometry, structure and solidity of copper nets

There are four types of copper netting presently used in the aquaculture industry. *Expanded copper-nickel* (Fig. 2.2a) was originally employed in inshore fish farms in 1970s (Ansuini and Huguenin, 1978; Huguenin et al., 1981; Powell, 1976). It is made of 90% copper and 10% nickel and is available in a wide range of openings and gauges (NAAMM EMMA557, 1999; WHEA, 1984). The *chain-link woven brass* (Fig. 2.2b) is a composition of 65% copper and 35% zinc. It has been used since the 1990s inshore, and has been recently adapted for offshore farming (Celikkol et al., 2010; DeCew et al., 2010a). New material
designs, which have potential for large offshore operations, include welded silicon-bronze (Fig. 2.2c) and woven silicon-bronze (Fig. 2.2d) composed of 97% copper with 3% silicon. Since nylon netting is widely used in marine aquaculture, nets of this type (Fig. 2.2e) are included in the present study to compare the hydrodynamic performance of polymer nets with that of copper nets. The list of investigated net panels is provided in Table 2.1.

Hydrodynamic performance of nets is often characterized in terms of solidity (Aarsnes et al., 1990; Balash et al., 2009; Lader and Enerhaug, 2005; Zhan et al., 2006), defined as the ratio of projected area $A_p$ (normal to the net plane) of all threads to the outline area of the entire net panel $A$:

$$S = \frac{A_p}{A}$$

(2.1)

For the rectangular knotless mesh, the analytical formula for solidity is

$$S = \frac{(L_1 + L_2) \cdot d - d^2}{L_1 \cdot L_2}$$

(2.2)

![Fig. 2.2. Four types of copper netting and a sample of nylon knotless square net.](image-url)
where \( d \) is the average diameter of the thread, \( L_1 \) and \( L_2 \) are the distances between the axes of symmetry of two adjacent parallel threads in two perpendicular directions (Fig. 2.3a).

The total length of all threads in the \( a \times b \) rectangular panel (Fig. 2.4a) can be found as

\[
L = a + a \cdot b \cdot \frac{L_1 + L_2}{L_1 \cdot L_2} + b
\]  

(2.3)

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Netting material</th>
<th>Mesh type</th>
<th>Manufacturer</th>
<th>Mesh dimensions</th>
<th>Twine diameter</th>
<th>Analytical solidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-14</td>
<td>Nylon</td>
<td>Rectangular knotless</td>
<td>NET Systems, Inc.</td>
<td>14.00 x 13.50 mm</td>
<td>1.24 mm</td>
<td>17.2%</td>
</tr>
<tr>
<td>Nylon-26</td>
<td>Nylon</td>
<td>Rectangular knotless</td>
<td>NET Systems, Inc.</td>
<td>25.58 x 26.16 mm</td>
<td>2.65 mm</td>
<td>20.8%</td>
</tr>
<tr>
<td>Woven-3</td>
<td>Silicon-Bronze (SeaWire)</td>
<td>Rectangular knotless</td>
<td>Luvata Appleton</td>
<td>3.11 x 3.55 mm</td>
<td>0.49 mm</td>
<td>27.4%</td>
</tr>
<tr>
<td>Welded-25</td>
<td>Silicon-Bronze (SeaWire)</td>
<td>Rectangular knotless</td>
<td>Luvata Appleton</td>
<td>25.45 x 25.4 mm</td>
<td>2.05 mm</td>
<td>15.5%</td>
</tr>
<tr>
<td>ChainLink-29</td>
<td>Yellow Brass (UR30)</td>
<td>Chain-link diamond</td>
<td>Southwestern Wire, Inc.</td>
<td>20 x 25 diamonds*</td>
<td>2.50 mm</td>
<td>17.3%</td>
</tr>
<tr>
<td>ChainLink-44</td>
<td>Yellow Brass (UR30)</td>
<td>Chain-link diamond</td>
<td>CODELCO</td>
<td>14 x 15.5 diamonds*</td>
<td>4.00 mm</td>
<td>18.0%</td>
</tr>
<tr>
<td>Expanded-24</td>
<td>Copper-Nickel Alloy</td>
<td>Flattened expanded</td>
<td>Expanded Solutions LLC</td>
<td>15.11 x 30.48 x 25.91^ mm</td>
<td>1.63^ mm</td>
<td>23.9%</td>
</tr>
</tbody>
</table>

* The number of diamonds for 0.915 x 0.935 m^2 net panel (Fig. 2.4b)

Parameters are given in the order \( W_x \times L_0 \times W_1 \times L_4 \) (Fig. 2.4c)

Strand width is \( d = 1.62 \text{ mm} \) and strand thickness is \( t = 0.81 \text{ mm} \)

---

**Fig. 2.3.** Geometry of (a) rectangular mesh and (b) square mesh cells.
In the special case of the square knotless mesh \( (L_1 = L_2 \equiv L, \text{ Fig. 2.3b}) \), solidity can be expressed as

\[
S = \frac{2 \cdot L \cdot d - d^2}{L^2}
\]

(2.4)

(a) Knotless rectangular mesh

(b) Chain-link diamond mesh. The detailed view shows how the actual geometry is approximated with idealized rhombus

(c) Expanded metal mesh

Fig. 2.4. Geometry of a rectangular net panel with rectangular knotless, chain-link diamond and expanded metal meshes.
The total length of all threads in the $a \times b$ rectangular panel is given by

$$L_t = a + \frac{2 \cdot a \cdot b}{L} + b \quad (2.5)$$

In the case of chain-link diamond mesh in the $a \times b$ rectangular panel having $X$ and $Y$ diamonds in two perpendicular directions (Fig. 2.4b), the solidity is given by

$$S = 2 \cdot \sqrt{\left(\frac{X}{a}\right)^2 + \left(\frac{Y}{b}\right)^2} \cdot d \quad (2.6)$$

Note that the number of diamonds in two perpendicular directions, $X$ and $Y$, is conventionally used in fencing industry to characterize metal chain-link meshes. These parameters are related to the diamond mesh bar length, $L$, as

$$L = 0.5 \cdot \sqrt{\left(\frac{a}{X}\right)^2 + \left(\frac{b}{Y}\right)^2} \quad (2.7)$$

The total length of all threads in the $a \times b$ rectangular panel is

$$L_t = \frac{a \cdot b \cdot S}{d} \quad (2.8)$$

which can be expressed in terms of the number of diamonds as

$$L_t = 2 \cdot X \cdot Y \cdot \sqrt{\left(\frac{a}{X}\right)^2 + \left(\frac{b}{Y}\right)^2} \quad (2.9)$$

Formula (2.8) provides the total length of copper wires as observed in a 2D plane, and is appropriate for calculating the projected area of chain-link meshes. However, for manufacturing purposes (and for evaluation of weight), the actual length of all wire, taking into account the 3D nature of intertwines, is needed. The estimate of such length can be obtained by the analysis of 3D solid models of the mesh (a similar approach to extract physical properties from a geometric model is discussed in Schwing, 1987; Wesley, 1980). Such an analysis was performed in the CAE software package SolidWorks 2010. The estimate of the total length is

$$L_t^{3D} = 2 \cdot X \cdot Y \cdot \sqrt{\left(\frac{a}{X}\right)^2 + \left(\frac{b}{Y}\right)^2} + 4.37 \cdot d \cdot (X + 2 \cdot X \cdot Y + Y) \quad (2.10)$$
Expanded mesh nets are manufactured by simultaneous indentation and expansion of a metal sheet (NAAMM EMMA557, 1999). The resulting geometry is characterized by six parameters defined in Fig. 2.4c. The analytical formula for solidity of such a mesh is quite cumbersome:

\[
S = \frac{L_o \cdot W_o - 2 \cdot L_i \cdot W_i + W_i^2 \cdot \cot \theta}{L_o \cdot W_o}
\]

(2.11)

where \( \theta \) is the angle between the strand and the long axis of diamond, so that the cotangent of \( \theta \) is

\[
\cot \theta = \frac{(2 \cdot L_i - L_o) \cdot \sqrt{(2 \cdot L_i - L_o)^2 + W_o^2 - 4 \cdot d^2 + 2 \cdot d \cdot W_o}}{W_o \cdot \sqrt{(2 \cdot L_i - L_o)^2 + W_o^2 - 4 \cdot d^2 - 2 \cdot d \cdot (2 \cdot L_i - L_o)}}
\]

Note that the approximation of actual mesh geometry with fillets (Fig. 2.5a) by an ideal geometry with sharp corners (Fig. 2.5b) does not affect the accuracy of the formula (2.11) as was established by analyzing both cross-sections in SolidWorks 2010. The total length of all strands in the \( a \times b \) rectangular panel of expanded mesh is given by formula (2.8).

The analytical formulae (2.2)-(2.11) were obtained using the assumption of a perfect net geometry. If more accurate estimates of net solidity or other geometric parameters are needed, more advanced characterization techniques can be used. For example, digital image processing (DIP) which is traditionally employed for characterization of microstructure of composite materials (see, for example, Al-Raoush and Alshibli, 2006; Marinoni et al., 2005; Tsukrov et al., 2005) can be used to analyze complicated mesh geometry. To perform such a characterization, digital images of the considered net panels shown in Fig. 2.2 were taken with a high-resolution digital camera, pre-processed with Adobe Photoshop to convert color images to black-and-white binary images, and processed

(a) actual geometry with fillets  (b) idealized diamond shape with sharp corners

Fig. 2.5. Expanded mesh geometry idealization.
in MATLAB to calculate the ratio of black pixels to the total number of pixels in the image. Table 2.2 compares the DIP evaluations of solidity to the predictions obtained with analytical formulae. It can be seen that the analytical estimates of solidity are within 4% of the DIP estimates, which should be sufficient for most applications.

Note that traditional metal manufacturer standards (e.g. NAAMM EMMA557, 1999) provide data on open area of panels which cannot be directly used to evaluate the solidity required for accurate drag force predictions. For example, the standard expanded carbon steel style \( \frac{3}{4} \#10 \) net has an actual solidity of 31.1%, while the Standard lists an open area of 72%, which corresponds to solidity of 28%.

![Table 2.2. Solidities of the selected net panels.](image)

<table>
<thead>
<tr>
<th>Net type</th>
<th>Solidity (DIP), %</th>
<th>Solidity (analytical), %</th>
<th>Relative Difference*, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-14</td>
<td>17.23</td>
<td>17.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Nylon-26</td>
<td>20.56</td>
<td>20.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Woven-3</td>
<td>26.81</td>
<td>27.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Welded-25</td>
<td>15.12</td>
<td>15.5</td>
<td>2.5</td>
</tr>
<tr>
<td>ChainLink-29</td>
<td>17.17</td>
<td>17.3</td>
<td>0.8</td>
</tr>
<tr>
<td>ChainLink-44</td>
<td>18.73</td>
<td>18.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Expanded-24</td>
<td>24.23</td>
<td>23.9</td>
<td>1.4</td>
</tr>
</tbody>
</table>

*Relative difference was calculated as \( \delta = \left| \frac{S_{\text{analytical}} - S_{\text{DIP}}}{S_{\text{DIP}}} \right| \times 100\% \)

2.3. Review of analytical predictions of drag forces on netting

Substantial research has been done over the past few decades by different authors to develop empirical models of hydrodynamic response of different kinds of netting. In this section, several available models for estimation of the net panel drag coefficient, \( C_D \), are reviewed. The review covers only normal drag coefficients and does not include lift force estimates. Since different authors used different parameters and notation, all formulae are converted to a single format and notation system.

Consider net panels placed in a current directed perpendicular to the plane of the net panel. From dimensional analysis, the drag force acting on such a panel can be represented as

\[
F_D = \frac{1}{2} \cdot A_p \cdot C_D \cdot \rho \cdot V^2
\]  

(2.12)
where $A_p$ is the projected area of the net panel, $C_D$ is the projected area drag coefficient, $\rho_w$ is the density of the fluid (water), and $V$ is the free-stream velocity, see, for example, Kawakami (1964). Note that some publications use the outline area of the panel, $A$, instead of the projected area of all net strands, $A_p$, which leads to a different value of the drag coefficient (by a solidity dependent multiplier). In our review, we converted their results to the projected area drag coefficient values.

Estimates of drag coefficient for square meshes provided by Milne (1972) are

\begin{align}
C_D &= 1.0 + 2.73 \cdot \left( \frac{d}{L} \right) + 3.12 \cdot \left( \frac{d}{L} \right)^2, \quad \text{for knotless net} \tag{2.13a} \\
C_D &= 1.0 + 3.77 \cdot \left( \frac{d}{L} \right) + 9.37 \cdot \left( \frac{d}{L} \right)^2, \quad \text{for knotted net} \tag{2.13b}
\end{align}

where $d$ is the diameter of the strand and $L$ is the mesh bar length, as in Fig. 2.3. These formulas can be converted to provide the drag coefficient in terms of solidity utilizing the expression $S = 2 \cdot d / L$ (Milne, 1972):

\begin{align}
C_D &= 1.0 + 1.365 \cdot S + 0.780 \cdot S^2, \quad \text{for knotless net} \tag{2.14a} \\
C_D &= 1.0 + 1.885 \cdot S + 2.343 \cdot S^2, \quad \text{for knotted net} \tag{2.14b}
\end{align}

A different set of empirical expressions was proposed by Aarsnes et al. (1990). The authors performed a study of plane nets and established formulas for drag coefficient as a function of solidity and angle of attack (angle between the current direction and the normal to a net plane). For the normal to the plane currents (angle of attack $\alpha = 90^\circ$), the drag coefficient can be calculated as

\begin{equation}
C_D = 2 \cdot \frac{d}{L} - 4.96 \cdot \left( \frac{d}{L} \right)^3 + 109.6 \cdot \left( \frac{d}{L} \right)^3 \tag{2.15}
\end{equation}

which in terms of solidity, $S = 2 \cdot d / L$, yields

\begin{equation}
C_D = 1.0 - 1.24 \cdot S + 13.7 \cdot S^2 \tag{2.16}
\end{equation}

In the work of Tsukrov et al. (2003), a finite element model for simulating response of a net panel to the environmental forces was proposed based on the modification of Morison's
equation (Morison et al., 1950). In this model, the hydrodynamic force was normalized per unit strand length of the netting. In the case of steady current and no wave load, this force is given by

\[ F_{D} = \frac{1}{2} \cdot d \cdot C_{D} \cdot \rho_{w} \cdot V^{2} \]  \hspace{1cm} (2.17)

where \( C_{D} \) depends on the value of Reynolds number (Choo and Casarella, 1971; DeCew et al., 2010b):

\[
C_{D} = \begin{cases} 
\frac{8 \cdot \pi}{\text{Re}_{e} \cdot s} (1 - 0.87 \cdot s^{-2}) & (0 < \text{Re}_{e} \leq 1) \\
1.45 + 8.55 \cdot \text{Re}_{e}^{-0.50} & (1 < \text{Re}_{e} \leq 30) \\
1.1 + 4 \cdot \text{Re}_{e}^{-0.50} & (30 < \text{Re}_{e} \leq 2.33 \cdot 10^{5}) \\
-3.41 \cdot 10^{6} \cdot (\text{Re}_{e} - 5.78 \cdot 10^{5}) & (2.33 \cdot 10^{5} < \text{Re}_{e} \leq 4.92 \cdot 10^{5}) \\
0.401 \cdot \left(1 - \frac{\text{Re}_{e}}{5.99 \cdot 10^{5}}\right) & (4.92 \cdot 10^{5} < \text{Re}_{e} \leq 10^{7})
\end{cases} \hspace{1cm} (2.18)

\[ s = -0.077215655 + \ln \left(\frac{8}{\text{Re}_{e}}\right), \]

\( \text{Re}_{e} = \rho_{w} \cdot d \cdot V / \mu \) is the Reynolds number, and \( \mu \) is the dynamic viscosity. Thus, for this approach, constant value of \( C_{D} \) (independent from the free-stream velocity values) cannot be established. However, for a typical net mesh geometry subjected to a current \( 0.01 < V < 10 \text{ m/s} \), the Reynolds number is in the range: \( 30 < \text{Re}_{e} < 2.33 \cdot 10^{5} \) and \( C_{D} \) is given by the following expression

\[ C_{D} = (1.1 + 4.0 \cdot \text{Re}_{e}^{-1/2}) \cdot \frac{L_{y} \cdot d}{A_{p}} \]  \hspace{1cm} (2.19)

Zhan et al. (2006) performed experimental studies and proposed the following expression for the drag coefficient

\[ C_{D} = 1.0 + \frac{C_{1}}{V} + C_{2} \cdot S + C_{3} \cdot S^{2} \]  \hspace{1cm} (2.20)

In the case of square diamond mesh, the coefficients are \( C_{1} = 0.137, C_{2} = 1.002, C_{3} = 2.230 \).
Balash et al. (2009) proposed both an analytical model and an adjusted formula based on the experimental results. The analytical formula uses the drag coefficient for circular cylinders, $C_{D}^{0}$, from White (1974)

$$C_{D} = \frac{C_{D}^{0}}{(1 - S)^{2}}$$

(2.21)

where $C_{D}^{0} = 1 + 10 \text{Re}^{-2/3}$ for $\text{Re} \leq 5 \cdot 10^{3}$. Their corrected formula obtained by the least squares fitting of experimental data is

$$C_{D} = C_{D}^{0} \cdot \left( 8.03S - 0.74 + \frac{0.12}{S} \right)$$

(2.22)

The experimentally obtained values of normal drag coefficient for the tested net panels (listed in Table 2.1) are compared with all these models in Section 2.5. We would like to mention that these models are only a subset of a larger number of studies available in the literature (see Fredheim, 2005; Le Bris and Marichal, 1998; Wan et al., 2004; and others).

2.4. Experimental studies of normal drag of copper net panels

For copper nets, the dependence of drag forces on solidity is expected to be different from that of traditional nylon netting because of the difference in material stiffness, surface roughness, and strand arrangements. A laboratory study was conducted to evaluate normal drag coefficients of copper nets with different solidities. All experiments were performed in the wave/tow tank facility of the University of New Hampshire. The dimensions of the tow tank are $36.6 \times 3.66 \times 2.44$ m, so that net panels with dimensions up to $1.0 \times 1.0$ m can be tested without interference with the tank walls (Swift et al., 2006). Mesh geometry of each panel was characterized by taking measurements of mesh diameter and bar length at five random locations with digital calipers having resolution of 0.01 mm. Solidity values calculated using this data were later verified by comparing to the DIP estimates, see Table 2.2.

For this study, net panels were fabricated and inserted into a welded stainless steel frame made of 0.5" Schedule 40 pipe. They were mounted on a tow carriage as schematically shown in Fig. 2.6. The setup included a tow post (1) that was rigidly fixed to the tow
carriage in a vertical position with a load cell (2) attached to the bottom end of the post. The post was made of the aluminum 25 mm square tube, inserted into an airfoil profile to reduce effects of the wake disturbance on the measurements. A load cell was attached to 2.5 mm nylon line that was joined to the four-point bridle made of the same material. The bridle was attached to the net panel frame (3) suspended from the tow carriage (4) by two 10 mm vertical rods (5) pin connected on both ends.

During the testing, each net panel was fully submerged (ca. 0.7 m) to avoid generation of surface waves and their interference with the measurements. Each net panel was oriented normal to the towing direction (angle of attack $a = 90^\circ$) and towed at constant velocities ranging from 0.1 m/s to 1.0 m/s in 0.1 m/s increments with three repetitions. Tow carriage velocity was monitored at each run using light gate sensors set at three locations along the towing path. The wait time between each tow was 1-5 minutes to allow water disturbance to dissipate. For comparison purposes, the same tests were also performed on two nylon nets with similar solidities and geometry.

The data acquisition system used for this study consisted of a single tension/compression load cell (SENTRAN ZB3-50) with a capacity of 222.5 N (50 lbs). The load cell

Fig. 2.6. Tow carriage set-up. Towing direction is schematically shown with bold arrows.
was connected to a National Instruments data acquisition board through a 10 V strain gage input module (DATAFORTH DSCA38-05) with a data acquisition frequency of 10 Hz. Data input was calibrated through a series of weight measurements with increments of 22 N (5 lbs). Before starting the tow tests for a new net panel, the load cell was checked with no load applied (drift check) and with 160 N (36 lbs) applied (input gain calibration check) to assure accuracy of the measurements. The same procedure was followed at the end of the tow tests for each panel to ensure that the setup was consistent throughout the test. Data processing was conducted with MATLAB script utilizing the algorithm shown in Fig. 2.7. An example of the obtained data plot is shown in Fig. 2.8.

The experimentally obtained plots of drag force vs. current velocity for different net types are presented in Fig. 2.9. They were produced by subtracting the force acting solely on the frame (measured in a separate set of experiments) from the total recorded force. In addition to the data points, continuous curves produced by a least squares quadratic regression are shown. Note that the force for the expanded mesh at 1.0 m/s could not be measured due to the load cell limitation (force was higher than the maximum load of load cell). The projected

![Data processing algorithm](image-url)

**Fig. 2.7.** Data processing algorithm.
**Fig. 2.8.** Data plot example illustrating the variation of the acquired time series.

**Fig. 2.9.** Drag force vs. current velocity for different net types. For clarity, plotted data points represent averages of the three repetitions at each towing velocity.
behavior is shown by the dashed line. The results of our study are consistent with the previously reported data for galvanized steel and copper chain-link (DeCew et al., 2007) and expanded metal (WHEA, 1984) panels.

To confirm that there is no interference from the tank walls and contribution of the net frame is consistent, an additional experiment was conducted with a 0.5×0.5 m² panel. The same data processing procedure was followed (see Fig. 2.7), and the determined value of the drag coefficient was within 1.2% from the one obtained from the 1.0×1.0 m² net panel.

2.5. Discussion of experimental results

The experimental data presented in Fig. 2.9 can be processed to obtain estimates of the drag coefficient of the nets. Assuming that the forces acting on the net are related to the drag coefficients by expression (2.12), the dependence of drag coefficients on the free stream velocity (Fig. 2.10) and on the Reynolds number (Fig. 2.11) can be established. Examination of the plots results in the following observations:

- Drag coefficients for each net panel reach steady values for current velocities of 0.4 – 0.5 m/s and stay approximately constant up to 1.0 m/s (highest tested velocities). This is attributed to transition of the flow regime from viscous laminar at low currents to the developed turbulent flow at higher velocities, as discussed, for example, in Kundu and Cohen, 2008; Sumer and Fredsøe, 2006; for the case of smooth cylinders. Also, note that the relative accuracy of measurements increases at higher values of drag force. In the presented study, the average standard error of force measurements for all considered net panels tested at 0.1 m/s is approximately 20%, while at 1.0 m/s the average standard error reduces to 0.3%.

- For nets of different geometries and materials, there is no immediately observed dependence of the drag coefficient on the values of solidity. For example, drag coefficient of the nylon net with 17.2% solidity (denoted as Nylon-14) is about two times higher than that of the copper net (ChainLink-29) with 17.3% solidity. At the same time, the drag coefficients of Welded-25 (S = 15.5%) and Woven-3 (S = 27.4%) are very close to each other.
Fig. 2.10. Plot of drag coefficient vs. current velocity for different net types.

Fig. 2.11. Plot of drag coefficient vs. Reynolds number for different net types.
• The experimental results do not reveal any direct dependence of the drag coefficient on either physical mesh size or Reynolds number of the net strands. One can analyze the nettings considered in the previous paragraph: the steady values of drag coefficient are very similar for *Welded-25* and *Woven-3*, but for *Welded-25* (mesh size 25 mm, strand diameter 2.05 mm) the range of Reynolds numbers is $900 < Re_n < 2,300$, while for *Woven-3* (mesh size 3 mm, strand diameter 0.49 mm) the range is $275 < Re_n < 550$ (see Fig. 2.11).

• Copper nets exhibit significantly lower $C_D$ as compared to nylon nets of comparable solidity. The only exception is *Expanded-24* mesh that has substantially different strand geometry. This is attributed to the difference between drag coefficients for different strand geometries (thin plates vs. circular cylinders), see Hoerner, 1965; Lindsey, 1937.

It appears that forces on nets may depend not only on solidity (projected area) but also on the ratio of the turbulence region area around net threads to the outline area of a net panel. Thus, for the same solidity, nets with larger mesh size will have larger areas of undisturbed flow resulting in lower drag force on such nets (compare *Nylon-14* with $S = 17.2\%$ vs. *Nylon-26* with $S = 20.8\%$). At the same time, strands with higher surface roughness will generate larger turbulence regions and, thus, higher drag (see also discussion in Balash et al., 2009). The latter effect can be observed when comparing drag coefficients of nylon (rough) and copper (smooth) nets. Thus, proper description of nets should include, in addition to solidity, information on the mesh geometry and strand roughness. Note that some studies of the surface roughness effect on the drag forces acting on the circular cylinders are available in the literature, see, for example, Achenbach (1971); Buresti (1981); Theophanatos and Wolfram (1989); Wolfram and Naghipour (1999).

To obtain the values of drag coefficients representative for the entire tested range of free-stream velocities, the quadratic regression curves presented in Fig. 2.9 were utilized. From the coefficients of parabolic representation, $F_D = K \cdot V^2$, the drag coefficients were extracted according to

$$C_D = \frac{2 \cdot K}{A_r \cdot \rho_w} \quad (2.23)$$
Table 2.3. Experimentally obtained normal drag coefficients for the tested net panels.

<table>
<thead>
<tr>
<th>Tow Test</th>
<th>S, %</th>
<th>Representative Drag Coefficient</th>
<th>Correlation Coefficient, $r^2$</th>
<th>Average Drag Coefficient*</th>
<th>Standard Error*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-14</td>
<td>17.2</td>
<td>1.508</td>
<td>0.9997</td>
<td>1.516</td>
<td>0.004 (0.24%)</td>
</tr>
<tr>
<td>Nylon-28</td>
<td>20.8</td>
<td>1.449</td>
<td>0.9998</td>
<td>1.419</td>
<td>0.007 (0.46%)</td>
</tr>
<tr>
<td>Woven-3</td>
<td>27.4</td>
<td>1.067</td>
<td>0.9999</td>
<td>1.093</td>
<td>0.004 (0.37%)</td>
</tr>
<tr>
<td>Welded-25</td>
<td>15.5</td>
<td>0.956</td>
<td>0.9994</td>
<td>0.993</td>
<td>0.007 (0.66%)</td>
</tr>
<tr>
<td>ChainLink-29</td>
<td>17.3</td>
<td>0.785</td>
<td>0.9978</td>
<td>0.736</td>
<td>0.009 (1.21%)</td>
</tr>
<tr>
<td>ChainLink-44</td>
<td>18.0</td>
<td>0.716</td>
<td>0.9978</td>
<td>0.868</td>
<td>0.007 (1.07%)</td>
</tr>
<tr>
<td>Expanded-24</td>
<td>23.9</td>
<td>1.705</td>
<td>0.9993</td>
<td>1.628</td>
<td>0.014 (0.87%)</td>
</tr>
</tbody>
</table>

*Based on the set of 21 data points (7 towing velocities with three repetitions in the range $0.4 \leq V \leq 1.0\, m/s$) for each tow test, except for the Expanded-24, for which there were only 18 data points.

The extracted values and the corresponding correlation coefficients, $r^2$, are given in Table 2.3. In addition, average values of the drag coefficients presented in Fig. 2.10 are provided for the range of velocities $0.4 \leq V \leq 1.0\, m/s$ with the corresponding standard errors. It is interesting to note that experimentally obtained drag coefficients for chain-link meshes are lower than those of smooth cylinders in the same range of Reynolds numbers (ca. 1.21, see Hoerner, 1965). We attribute this to the three-dimensionality of the chain-link geometry, which may cause streamlining of the flow.

Table 2.4 presents a comparison of the experimental data with the analytical predictions of drag coefficients discussed in Section 2.3. The comparison is provided for the values of drag coefficient at $V = 1\, m/s$ (note that the current velocity is required as an input parameter as some of the analytical models are velocity dependent). The comparison for the Expanded-24 mesh is not provided because of its distinctive geometric properties resulting in a very different fluid flow pattern.

It can be seen that none of the models provide accurate predictions for all of the considered nets. The discrepancies vary from -20% to 114%. As expected, analytical predictions demonstrate better correlation for nylon nets because they were developed for this type of material. In fact, four of the models (Milne-1972, Aarsnes-1990, Zhan-2006 and Balash-2009-experimental) are based on the experimental measurements of the specific net types for which these models are accurate.
Table 2.4. Comparison of experimental data to the predictions by different analytical models at 1 m/s. The references to corresponding formulae in Section 2.3 are provided in parentheses.

<table>
<thead>
<tr>
<th>Tow Test</th>
<th>( Re _x )</th>
<th>Experimental</th>
<th>Milewski-1972 (2.14a)</th>
<th>Aarnes-1990 (2.16)</th>
<th>Tzokov-2003 (2.19)</th>
<th>Zhao-2008 (2.20)</th>
<th>Balash-2009 (2.21)</th>
<th>Balash-2009 (2.22)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nylon-14</td>
<td>1,390</td>
<td>1.499</td>
<td>1.258</td>
<td>1.192</td>
<td>1.284</td>
<td>1.375</td>
<td>1.575</td>
<td>1.446</td>
</tr>
<tr>
<td>( S = 17.2% )</td>
<td></td>
<td></td>
<td>-16%</td>
<td>-20%</td>
<td>-14%</td>
<td>-8%</td>
<td>5%</td>
<td>-4%</td>
</tr>
<tr>
<td>Nylon-26</td>
<td>3,196</td>
<td>1.442</td>
<td>1.318</td>
<td>1.335</td>
<td>1.272</td>
<td>1.442</td>
<td>1.668</td>
<td>1.576</td>
</tr>
<tr>
<td>( S = 20.8% )</td>
<td></td>
<td></td>
<td>-9%</td>
<td>-7%</td>
<td>-12%</td>
<td>0%</td>
<td>16%</td>
<td>9%</td>
</tr>
<tr>
<td>Woven-3</td>
<td>549</td>
<td>1.072</td>
<td>1.433</td>
<td>1.689</td>
<td>1.375</td>
<td>1.579</td>
<td>2.179</td>
<td>2.181</td>
</tr>
<tr>
<td>( S = 27.4% )</td>
<td></td>
<td></td>
<td>34%</td>
<td>58%</td>
<td>28%</td>
<td>47%</td>
<td>103%</td>
<td>103%</td>
</tr>
<tr>
<td>Welded-25</td>
<td>2,299</td>
<td>0.970</td>
<td>1.230</td>
<td>1.137</td>
<td>1.262</td>
<td>1.348</td>
<td>1.481</td>
<td>1.352</td>
</tr>
<tr>
<td>( S = 15.5% )</td>
<td></td>
<td></td>
<td>27%</td>
<td>17%</td>
<td>30%</td>
<td>39%</td>
<td>53%</td>
<td>39%</td>
</tr>
<tr>
<td>ChainLink-29</td>
<td>2,803</td>
<td>0.758</td>
<td>1.259</td>
<td>1.196</td>
<td>1.176</td>
<td>1.377</td>
<td>1.535</td>
<td>1.410</td>
</tr>
<tr>
<td>( S = 17.3% )</td>
<td></td>
<td></td>
<td>66%</td>
<td>58%</td>
<td>55%</td>
<td>82%</td>
<td>103%</td>
<td>86%</td>
</tr>
<tr>
<td>ChainLink-44</td>
<td>4,485</td>
<td>0.721</td>
<td>1.271</td>
<td>1.221</td>
<td>1.164</td>
<td>1.390</td>
<td>1.542</td>
<td>1.422</td>
</tr>
<tr>
<td>( S = 18.0% )</td>
<td></td>
<td></td>
<td>76%</td>
<td>69%</td>
<td>61%</td>
<td>93%</td>
<td>114%</td>
<td>97%</td>
</tr>
</tbody>
</table>

*Relative difference was calculated as \( \delta = \frac{(C_D^* - C_D)}{C_D^*} \times 100\% 

Note that an analogous comparison was performed for the averaged (over the considered range of velocities) \( C_D \) values from both experimental and analytical data. A similar trend was observed: discrepancies were in the range from -21% to 133%. Thus, none of the considered analytical models developed for nylon nets can be immediately applied to predict the hydrodynamic response of copper netting.

2.6. Conclusions on normal drag coefficients of copper alloy nets

Mesh geometry of the major types of copper nets currently used in the marine aquaculture were analyzed and formulae for the solidity and strand length were proposed in Section 2.2. Tow tests on the square 1.0x1.0 \( m^2 \) net panels of several net types were conducted to determine normal drag coefficients in steady currents. The obtained values for range of free-stream velocities \( 0.1 < V < 1 \) m/s are given in Table 2.3.
It was observed that copper nets exhibit significantly lower drag resistance in steady currents than nylon nets of the comparable solidities. Thus, solidity alone cannot be used as a sufficient parameter to predict drag coefficients of nets made of different materials. Contribution of other factors such as type of the mesh geometry, strand flexibility and strand roughness should be taken into account. Proper description should include, in addition to solidity, information on the mesh type and strand geometry.

Comparison of the experimental data to several previously published analytical models was performed. None of the considered models can be directly applied to predict drag forces on copper nets. It is recommended that the experimentally obtained drag coefficients (Table 2.3) be used to evaluate such forces. Further studies are required to develop comprehensive hydrodynamic models for nets made of copper alloys.
Chapter 3. Corrosion and Biofouling Behavior of Copper Alloys in Natural Seawater

In this chapter, the results of corrosion and biofouling studies of eight copper alloys are reported. The specimens, deployed for a year at the Portsmouth Harbor (the North Atlantic Ocean), include tensioned and untensioned sets, as well as a set of specimens for seasonal deployments. The corrosion behavior is characterized by weight loss, optical microscopy, and SEM/EDX analyses. The biofouling performance is quantified in terms of the biomass accumulation. It is found that the 3-month corrosion rates for untensioned specimens are 2.4x higher than the rates from 12-month testing. The 12-month corrosion rates of tensioned specimens are 1.4x higher than the rates from untensioned testing. The biofouling resistance are found to be excellent for all but one alloy, which exhibits heavy fouling by barnacles.

3.1. Literature review on corrosion behavior of copper alloys in seawater

Copper has been used as sheathing on the ship hulls since 18th century (Peters, 1991). However, timber, steel and, recently, polymers and composites have been the primary structural materials used in marine applications. This is attributed to the availability, low cost and ease of manufacturing of these materials. At the same time, these materials have limited service life and require regular maintenance due to high rates of deterioration and low biofouling resistance in seawater (Moffatt & Nichol Engineers, 1983).

Development and utilization of copper alloy components for structural marine applications is being actively promoted by the industry as a viable alternative due to the reduced maintenance costs, prolonged service life, increased reliability and high recyclability (Hunt and Bellware, 1967; Todd, 1991). Utilization of structural components made of these materials may benefit such industries as traditional (oil and gas) and renewable (wind and tidal turbines) offshore energy, marine aquaculture, shipbuilding, and harbor protection.

To effectively design structures with copper alloy components, it is important to understand their corrosion and mechanical behavior under the service conditions in marine environment. Even though some data on the corrosion rates of certain copper alloys has
been available from the beginning of the 20th century (Scott, 1913), most of the systematic studies, especially, devoted to newly developed copper alloys, began to appear in the mid-1970s and early 1980s. The work of Efird (1975) documented the detailed study of the interrelation of biofouling and corrosion for several materials, including copper alloys, over the four-year test in natural seawater. In another publication by Efird and Anderson (1975), the authors discussed the corrosion rates of two cupronickel alloys based on the data from a 14-year exposure to natural seawater. Parvizi et al. (1988) published a comprehensive review of literature on corrosion behavior of 90/10 cupronickels in seawater. In a more recent work by Davies (1993), the author provided a detailed review of literature on the dezincification behavior of brasses. However, it seems that after that period relatively few new papers were published on seawater corrosion of copper alloys, in particular, with respect to the relative performance of different alloys in natural seawater. Some of the found papers include Bastos et al. (2008), Michel et al. (2011), Santos et al. (2006). A detailed review of electrochemical corrosion processes of unalloyed copper in seawater environment is given in Kear et al. (2004).

In this chapter, we discuss the results of a one-year field testing of corrosion and biofouling performance of several families of copper alloys, including brasses, cupronickels and bronzes. Section 3.2 provides information on the tested materials and their properties. Section 3.3 describes the deployment location and experimental setup. Uniform corrosion results for 3-month and 12-month exposures are presented in Section 3.4. The results of biofouling measurements are discussed in Section 3.5. Section 3.6 provides the optical microscopy and SEM/EDX data on localized corrosion damage.

3.2. Composition and properties of investigated copper alloys

Eight copper alloys and two reference materials (pure copper and carbon steel) were selected for the seawater corrosion studies. The designations and chemical composition of the materials are presented in Table 3.1. We compare the corrosion and biofouling performance of several important families of alloys: brasses, bronzes, and cupronickels. The
Table 3.1. Composition (in wt.%) of the materials.

<table>
<thead>
<tr>
<th>Denomination</th>
<th>Alloy type</th>
<th>UNS designation</th>
<th>Cu</th>
<th>Zn</th>
<th>Sn</th>
<th>Ni</th>
<th>Sb</th>
<th>P</th>
<th>Fe</th>
<th>Mn</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>Admiral brasses</td>
<td>0444*</td>
<td>64.2</td>
<td>34.7</td>
<td>0.62</td>
<td>0.39</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-2</td>
<td>Admiralty brasses</td>
<td>C44400</td>
<td>71.0</td>
<td>27.9</td>
<td>1.13</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br-3</td>
<td>C44500</td>
<td>70.8</td>
<td>28.0</td>
<td>1.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Br-4</td>
<td>Special brasses</td>
<td>C68800</td>
<td>73.4</td>
<td>22.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.54 Al, 0.32 Co</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>Copper nickel</td>
<td>C70600</td>
<td>87.4</td>
<td></td>
<td>10.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuNi-2</td>
<td>Nickel silver</td>
<td>C78400</td>
<td>60.6</td>
<td>21.1</td>
<td>18.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuSi-1</td>
<td>Silicon bronze</td>
<td>C85500</td>
<td>95.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.09 3.01 Si</td>
</tr>
<tr>
<td>CuTin-1</td>
<td>Tin bronze</td>
<td>C51900</td>
<td>94.0</td>
<td>5.90</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.04</td>
</tr>
<tr>
<td>Cu</td>
<td>Copper</td>
<td>C12200</td>
<td>99.96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steel‡</td>
<td>Reference materials</td>
<td>K02600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>&lt;0.24 C, &lt;0.4 Si, 0.04 S</td>
</tr>
</tbody>
</table>

* a commercial alloy without an exact UNS equivalent
‡ chemical composition was not analyzed, values from ASTM A283/A283M-12

sheet metal samples were manufactured by casting, followed by hot and cold rolling. The final thickness of the sheets after cold rolling was 3 mm.

The mechanical properties were determined from the uniaxial tension tests conducted according to ASTM E8/E8M-08. All experiments were performed on the servohydraulic testing machine INSTRON 1350 with a digital controller. Force measurements were recorded using an integrated 100 kN force transducer. The data on deflections was recorded using two techniques, bonded resistance strain gages and digital image correlation (Drach et al., 2012b). This data was used to obtain the Young’s modulus (E), Poisson’s ratio (ν), and the ultimate tensile strength (σu). Table 3.2 shows the mechanical properties of the alloys, and their density. It can be seen that there are significant differences in the material properties between the alloys. This is explained by a wide range of their intended applications, see Table 3.3.

The surface roughness of the specimens (Table 3.4) was measured using a contact profilometer (Mahr Marsurf XCR 20, tip radius 2 μm) along the 5.6 mm paths parallel and perpendicular to rolling direction, following ASME B46.1. The grain sizes (Table 3.4) were
Table 3.2. Mechanical properties of tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E$, GPa</th>
<th>$v$</th>
<th>$\sigma_u$, MPa</th>
<th>Hardness, HV10</th>
<th>Temper</th>
<th>Initial Density, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>102</td>
<td>0.35</td>
<td>303</td>
<td>104</td>
<td>hard</td>
<td>8,289</td>
</tr>
<tr>
<td>Br-2</td>
<td>109</td>
<td>0.31</td>
<td>358</td>
<td>104</td>
<td>hard</td>
<td>8,397</td>
</tr>
<tr>
<td>Br-3</td>
<td>109</td>
<td>0.32</td>
<td>396</td>
<td>109</td>
<td>hard</td>
<td>8,394</td>
</tr>
<tr>
<td>Br-4</td>
<td>110</td>
<td>0.32</td>
<td>572</td>
<td>167</td>
<td>soft</td>
<td>7,982</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>124</td>
<td>0.30</td>
<td>340</td>
<td>116</td>
<td>hard</td>
<td>8,716</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>139</td>
<td>0.29</td>
<td>537</td>
<td>147</td>
<td>hard</td>
<td>8,586</td>
</tr>
<tr>
<td>CuSi</td>
<td>113</td>
<td>0.36</td>
<td>472</td>
<td>144</td>
<td>hard</td>
<td>8,411</td>
</tr>
<tr>
<td>CuTin</td>
<td>120</td>
<td>0.34</td>
<td>497</td>
<td>159</td>
<td>hard</td>
<td>8,632</td>
</tr>
<tr>
<td>Cu</td>
<td>132</td>
<td>0.27</td>
<td>401</td>
<td>97</td>
<td>hard</td>
<td>8,688</td>
</tr>
<tr>
<td>Steel</td>
<td>208</td>
<td>0.28</td>
<td>394</td>
<td>121</td>
<td>hard</td>
<td>7,692</td>
</tr>
</tbody>
</table>

Table 3.3. Typical applications of tested materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Typical Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>condenser and evaporator tubing, marine nets</td>
</tr>
<tr>
<td>Br-2</td>
<td>electrical and electronic connectors</td>
</tr>
<tr>
<td>Br-3</td>
<td>ship hulls, salt water piping systems, condenser and evaporator tubing</td>
</tr>
<tr>
<td>Br-4</td>
<td>connectors, relay springs, spectacle arms and hinges, decorative parts</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>welding wire, electrical motors, fasteners</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>stamped parts, electrical and electronic connectors</td>
</tr>
<tr>
<td>CuSi</td>
<td>plumbing tube, roofing, heat exchangers</td>
</tr>
<tr>
<td>CuTin</td>
<td>machine parts, fasteners, moderate strength structural components</td>
</tr>
<tr>
<td>Cu</td>
<td>machine parts, fasteners, moderate strength structural components</td>
</tr>
<tr>
<td>Steel</td>
<td>machine parts, fasteners, moderate strength structural components</td>
</tr>
</tbody>
</table>

Table 3.4. Roughness, grain size, and susceptibility to SCC and dezincification.

<table>
<thead>
<tr>
<th>Material</th>
<th>Roughness $R_z$, μm</th>
<th>Grain size, μm</th>
<th>SCC</th>
<th>Depth of dezincification, μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>1.28 ... 1.90</td>
<td>50 ... 55</td>
<td>no cracks</td>
<td>3</td>
</tr>
<tr>
<td>Br-2</td>
<td>1.20 ... 2.14</td>
<td>60 ... 65</td>
<td>no cracks</td>
<td>7</td>
</tr>
<tr>
<td>Br-3</td>
<td>1.39 ... 1.85</td>
<td>15 ... 250</td>
<td>no cracks</td>
<td>6</td>
</tr>
<tr>
<td>Br-4</td>
<td>0.68 ... 3.06</td>
<td>*</td>
<td>no cracks</td>
<td>735</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>1.29 ... 1.60</td>
<td>15 ... 40</td>
<td>no cracks</td>
<td>8</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>1.04 ... 2.93</td>
<td>30 ... 35</td>
<td>no cracks</td>
<td>65</td>
</tr>
<tr>
<td>CuSi</td>
<td>0.68 ... 3.06</td>
<td>15 ... 20</td>
<td>no cracks</td>
<td>13</td>
</tr>
<tr>
<td>CuTin</td>
<td>1.19 ... 1.36</td>
<td>15 ... 20</td>
<td>no cracks</td>
<td>no dealloying observed</td>
</tr>
<tr>
<td>Cu</td>
<td>0.71 ... 1.40</td>
<td>*</td>
<td>no cracks</td>
<td>no dealloying observed</td>
</tr>
</tbody>
</table>

* Grain size determination not possible because of heavy deformation
determined with an optical-light microscope by making linear intercepts of grain boundaries parallel to the rolling direction (see ASTM E112-10). Standardized laboratory corrosion tests were used to evaluate susceptibility to the localized corrosion damage: stress corrosion cracking, SCC, at moderate corrosiveness level according to ISO 6957; and dezincification in CuCl₂ solution according to ISO 6509. The results are shown in Table 3.4. None of the sheet materials was susceptible to SCC. The depth of dezincification was low for most materials except the Al-containing special brass Br-4 (high), and the Nickel Silver alloy CuNi-2 (moderate). Note that these two materials are among those not intended for marine applications.

3.3. Deployment location and field setup

Three studies were conducted to evaluate performance of the copper alloys in the marine environment: material loss in tensioned specimens, material loss in untensioned specimens, and biofouling resistance of untensioned specimens. The specimens of rectangular shape (180 × 50 × 3 mm³) were cut out of the metal sheets. Two 6-mm diameter holes were drilled in each specimen (Fig. 3.1) for attachment. Edges of the holes were countersunk on both faces of the plate to remove sharp edges. The specimens were marked using a metal stamp for identification purposes.

The untensioned specimens were secured with 3 mm plastic zip-ties and deployed in a rigid PVC frame. This design was chosen based on the previous studies examining biofouling (Greene and Grizzle, 2007). The copper alloy specimens were randomly distributed across two frames, as illustrated in Fig. 3.2a. For the biofouling resistance

![Fig. 3.1. Specimen geometry.](image-url)
studies, nylon specimens in the form of net panels (shown as square frames in Fig. 3.2a) were also included.

The tensioned setup consisted of a series of specimens secured to the deadweight on a seafloor, and loaded by a pair of buoys attached to the top specimen. The total height of the setup was such that the floats were permanently underwater, providing constant tension gradually varying from 640 N at the top to 615 N at the bottom. The variation in tension was due to the weight of specimens. The series were assembled at a fixed spacing of 55 ± 5 mm (edge to edge between the samples) using 1/8" Spectra 12-strand rope. Fig. 3.2b shows an example of the setup. Three such setups were used in the experiment.

All specimens were deployed near the mouth of Portsmouth Harbor at the University of New Hampshire Coastal Marine Laboratory (Fig. 3.3) for a total of 12 months. One set of untensioned specimens denoted as W in Fig. 3.2a was inspected every season to obtain shorter-term corrosion rates and their seasonal variation. At each recovery, the specimens were subjected to the same cleaning and inspection procedure, and re-deployed at the same

![Diagram of deployment setup](image-url)

**Fig. 3.2.** Schematics of the deployment setup for testing of copper alloy plates in marine environment: (a) untensioned; (b) tensioned. The set of untensioned specimens denoted as W was used for seasonal corrosion rate measurements.
positions. Table 3.5 presents the average values of temperature, salinity, dissolved oxygen concentration, and alkalinity, as well as the corresponding ranges over each seasonal deployment period.

Table 3.5. Summary data on environmental conditions (daily ranges and averages over the deployment period).

<table>
<thead>
<tr>
<th>Period</th>
<th>Temp., °C</th>
<th>Salinity, ppt</th>
<th>DO, mg/L</th>
<th>pH</th>
<th>Water depth, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>06/30/10 - 12/17/10</td>
<td>11.3</td>
<td>5.3 - 18.2</td>
<td>30.8</td>
<td>25.8 - 33.7</td>
<td>8.0</td>
</tr>
<tr>
<td>12/17/10 - 03/05/11</td>
<td>2.6</td>
<td>0.6 - 5.3</td>
<td>29.0</td>
<td>26.5 - 30.3</td>
<td>10.7</td>
</tr>
<tr>
<td>03/05/11 - 06/01/11</td>
<td>5.8</td>
<td>2.1 - 12.6</td>
<td>25.5</td>
<td>22.4 - 28.2</td>
<td>11.2</td>
</tr>
<tr>
<td>06/01/11 - 08/24/11</td>
<td>15.0</td>
<td>9.9 - 19.2</td>
<td>29.3</td>
<td>27.1 - 30.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

**Fig. 3.3.** Deployment location from Google Earth (43° 4' 19" N, 70°42' 37" W).
3.4. Uniform corrosion studies

3.4.1. Corrosion measurement procedure

The corrosion evaluation procedure included visual analysis, chemical cleaning with 10% sulfuric acid (following ASTM G1-03), digital imaging before and after cleaning, weight measurements, and data processing. Weight measurements were performed using mechanical triple beam scales (resolution of 0.1 g). The weight loss data for each of the specimens was converted to the uniform corrosion rate expressed in the units of thickness per year (ASTM G1-03):

$$\alpha = \frac{\Delta m}{\rho_0 \cdot A_0 \cdot t_D} \cdot \frac{365}{t_D}, \quad (3.1)$$

where $\Delta m$ is the weight loss of the specimen (in g), $\rho_0$ is the initial density of the material (g/μm²), $A_0$ is the initial surface area (μm²), and $t_D$ is the duration of exposure (days).

To evaluate the uncertainty in the measurements, the error propagation approach was applied (Sharpe, 2008). The following sources of uncertainty were considered: instrument errors (resolution, bias, linearity), and systematic errors (operator error, equipment variability). The Euclidean norm approximation for the relative uncertainty due to instrument errors is given by:

$$e_{\alpha} = \frac{e}{\alpha} = \frac{1}{\alpha} \sqrt{(u_{\Delta m} \cdot \frac{\partial \alpha}{\partial \Delta m})^2 + (u_\rho \cdot \frac{\partial \alpha}{\partial \rho})^2 + (u_A \cdot \frac{\partial \alpha}{\partial A})^2} = \sqrt{(\frac{u_{\Delta m}}{\Delta m})^2 + (\frac{u_\rho}{\rho})^2 + (\frac{u_A}{A})^2} \quad (3.2)$$

where $u_{\Delta m} = 71 \text{ mg}$, $u_{\rho} = 80 \text{ kg/m}^3$, $u_A = 65 \text{ mm}^2$, are the weight, density and surface area measurement uncertainties due to instrument errors reported in Drach et al. (2012a). Substituting these values into equation (3.2), we obtain the relative uncertainty estimate of ±2.7% for continuous 12-month deployment, and ±4.9% for interrupted seawater exposure. To minimize the systematic errors, a single operator performed all of the measurements using the same equipment. Where applicable, equipment calibration was checked before every measurement session. An example of measurements with the corresponding values of relative uncertainties for the set of specimens from the 12-month untensioned exposure is presented in Table 3.6.
Table 3.6. Example of the corrosion data for one of the specimen sets.

<table>
<thead>
<tr>
<th>Material</th>
<th>Original Weight, g</th>
<th>Surface Area, mm²</th>
<th>Weight loss after recovery, g</th>
<th>Apparent corrosion rate value, μm/year</th>
<th>Relative Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>228.7</td>
<td>19,749</td>
<td>2.8</td>
<td>17.4</td>
<td>2.7%</td>
</tr>
<tr>
<td>Br-2</td>
<td>232.2</td>
<td>19,708</td>
<td>2.8</td>
<td>17.2</td>
<td>2.7%</td>
</tr>
<tr>
<td>Br-3</td>
<td>223.1</td>
<td>19,052</td>
<td>2.7</td>
<td>17.2</td>
<td>2.8%</td>
</tr>
<tr>
<td>Br-4</td>
<td>221.7</td>
<td>19,691</td>
<td>0.6</td>
<td>3.9</td>
<td>11.8%</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>239.1</td>
<td>19,454</td>
<td>2.3</td>
<td>13.6</td>
<td>3.2%</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>232.6</td>
<td>19,372</td>
<td>4.5</td>
<td>27.5</td>
<td>1.9%</td>
</tr>
<tr>
<td>CuSi</td>
<td>228.6</td>
<td>19,468</td>
<td>2.3</td>
<td>14.3</td>
<td>3.2%</td>
</tr>
<tr>
<td>CuTin</td>
<td>243.1</td>
<td>19,728</td>
<td>1.9</td>
<td>11.1</td>
<td>3.9%</td>
</tr>
<tr>
<td>Cu</td>
<td>217.2</td>
<td>19,404</td>
<td>2.3</td>
<td>13.9</td>
<td>3.2%</td>
</tr>
<tr>
<td>Steel</td>
<td>207.1</td>
<td>19,483</td>
<td>23.7</td>
<td>160.8</td>
<td>1.0%</td>
</tr>
</tbody>
</table>

The effect of cleaning procedure was evaluated by performing a separate study on a set of virgin plate specimens. Each of the specimens was subjected to the cleaning procedure four times. Weight changes were recorded after each cleaning using an analytical microbalance (Denver instrument SI-413) with resolution of 1 mg. It was observed that for all of the tested materials (except for steel), the effect of cleaning was negligible and did not affect the measurements. To account for the weight loss due to cleaning, the measurements for steel specimens were adjusted as recommended in NACE RP0497-04.

3.4.2. Corrosion rates of copper alloys for the 12-month exposure

Three sets of specimens were subjected to 12 months of uninterrupted seawater exposure: one set in untensioned configuration and two sets under tension. The observed corrosion rates are summarized in Fig. 3.4 and the last two columns of Table 3.7. It can be seen that most of the alloys exhibit the corrosion rates similar to that of copper for both tensioned and untensioned configurations. Only one alloy (Br-4) corroded at a significantly lower rate, and one alloy (CuNi-2) displayed a relatively high corrosion rate. Performance of reference materials (copper and steel) is in good correlation with previously reported values (Francis, 2010; Schumacher, 1979). The measurement for CuNi-1 (13.8 μm/year) lies between the values of 6.9 and 19.5 μm/year obtained from Figure 1 of Efird and Anderson (1975) for the alloy of similar composition after one year in seawater under quiet and flowing (0.6 m/s) conditions, correspondingly. This result is as expected taking into account that the average flow velocities were 0.25 m/s at our deployment location.
Table 3.7. Uniform corrosion rates in μm/year.

<table>
<thead>
<tr>
<th>Material</th>
<th>3-month untensioned</th>
<th>12-month untensioned</th>
<th>12-month tensioned</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>39.9</td>
<td>17.4</td>
<td>22.7</td>
</tr>
<tr>
<td>Br-2</td>
<td>40.9</td>
<td>17.2</td>
<td>25.0</td>
</tr>
<tr>
<td>Br-3</td>
<td>42.7</td>
<td>17.2</td>
<td>25.8</td>
</tr>
<tr>
<td>Br-4</td>
<td>27.8</td>
<td>3.9</td>
<td>10.2</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>29.7</td>
<td>13.8</td>
<td>19.9</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>74.7</td>
<td>27.5</td>
<td>41.0</td>
</tr>
<tr>
<td>CuSi</td>
<td>36.3</td>
<td>14.3</td>
<td>19.9</td>
</tr>
<tr>
<td>CuTin</td>
<td>24.8</td>
<td>11.1</td>
<td>13.6</td>
</tr>
<tr>
<td>Cu</td>
<td>32.3</td>
<td>13.9</td>
<td>18.9</td>
</tr>
<tr>
<td>Steel</td>
<td>202</td>
<td>161</td>
<td>—</td>
</tr>
</tbody>
</table>

* average value from four seasonal observations on the same specimen
† average value from observations on different specimens of the same material

Fig. 3.4. Corrosion rates for continuous 12-month exposure. Horizontal lines represent the average values for tensioned specimens.

The observed values of uniform corrosion rates for tensioned specimens are substantially higher than those of untensioned specimens. Under the relatively low tensile force of 600 N (corresponding to average stress of ca. 4 MPa) applied in the experiment, the average difference is 39% or 6.8 μm/year. The most likely explanation of this phenomenon is the effect of dynamic loading on the specimens. It appears that the specimens in the
tensioned setup were subjected to varying tensile loading due to movements of the buoy caused by waves and tides. Since the mechanical properties of the base material and the adherent brittle corrosion layer (e.g. cuprous oxide, \( \text{Cu}_2\text{O} \), see Kear et al., 2004) differ, the applied mechanical loading produces the interface stresses which lead to microcracking of the protective corrosion layer. Microcracking facilitates access of seawater to unprotected base metal, and results in accelerated local corrosion.

Let us consider, for example, the untreated (immediately after recovery from seawater) specimen of CuSi from the 12-month uninterrupted tensioned exposure shown in Fig. 3.5a. It exhibits irregularities in the corrosion layer in the form of concentric circles around the attachment hole. This pattern is consistent with the distribution of principal strains in the specimen subjected to the tensile loads applied at the attachment holes, see Fig. 3.5b (the image was obtained by finite element simulations using SolidWorks Simulation module, www.solidworks.com). The microcracks due to interface stresses between dissimilar materials (base material and corrosion layer) open in the direction of the major principal strain. Under cyclic (fatigue) loading, this effect is manifested by the so-called beachmarks, see Dowling (2007).

**Fig. 3.5.** Surface condition and strains in the tensioned CuSi specimen: (a) image of the untreated surface right after recovery from seawater; (b) distribution of principal strains from finite element simulation. Only the left half of the specimen is shown.
Another potential mechanism is the material loss due to wear in the area where the attachment rope rubs against the surface of the specimen (distinct area to the left of the attachment hole in Fig. 3.5a). To investigate whether the wear at the attachment points produces significant contribution to material loss in the tensioned specimens, the digital image correlation (DIC) technique (Sutton et al., 2007) was utilized. Fig. 3.6a shows the wear mark to the left of the attachment hole in the cleaned Br-3 specimen. Fig. 3.6b presents the elevation contour map of the same area obtained by DIC analysis. The variations in the elevation are from -60 \( \mu m \) to 60 \( \mu m \) with respect to the average surface level as calculated by the VIC-3D software (www.correlatedsolutions.com). It can be seen that the depth of the groove due to friction with the attachment rope is less than 60 \( \mu m \). At the same time, if one assumes that all material loss difference between tensioned and untensioned specimens of Br-3 is due to wear in the contact area (illustrated in Fig. 3.6c) and there are four such areas on the two sides of the specimen near the attachment holes, the expected depth of the groove is

\[
d = \frac{\Delta m}{\rho} \frac{1}{4A} = \frac{1.6 \text{ g}}{0.0084 \text{ g/mm}^3} \cdot \frac{1}{4 \cdot 73.6 \text{ mm}^2} = 647 \mu m
\]  

(3.3)

Thus, the observed groove depth is about ten times smaller than what is required to account for the increased material loss. We conclude that wear at the attachment is not the primary mechanism responsible for the additional material loss in the tensioned specimens.

Fig. 3.6. Upper part of Br-3 specimen: (a) cleaned surface after seawater exposure; (b) contour map of surface elevation; (c) schematics with the contact wear area.
3.4.3. Corrosion rates of copper alloys for the 3-month exposure intervals

One set of the specimens was subjected to an interrupted seawater exposure. It was examined approximately every three months (the exact intervals are provided in Table 3.5), and then redeployed. The measured corrosion rates are presented in Fig. 3.7 and the first column of Table 3.7. It can be seen that the rates (recalculated as annual thickness reduction) exhibit significant scatter for each of the considered materials. There are several factors that could be responsible for such behavior: variation in environmental conditions, the duration of exposure (from 74 to 105 days), changes in seawater chemical composition, biofouling, stray electrical currents in the water. The measurements on biofouling are presented in Section 3.5, while the other factors are considered below.

Comparing information from Table 3.5 and Fig. 3.7, we observe that there is no direct correlation between the average values of seawater temperature, salinity, oxygen concentration, alkalinity and the corrosion rates of considered copper alloys during the 3-month seawater exposure. Taking into account the kinetics of corrosion layer formation (Jones, 1996), it may be expected that the environmental conditions during the period of

![Fig. 3.7. Corrosion rates for interrupted deployments. Numbers 1-4 indicate the deployment periods presented in the first column of Table 3.5. Horizontal lines represent the average values.](image)
rapid protective layer formation play more important role than during the rest of the period. However, comparison of the corrosion rates with the average values of the recorded environmental parameters over the first 15 days of each deployment period ($T_{15} = 15.4, 4.1, 2.8, 12.5^\circ C$; $Salinity_{15} = 30.2, 27.3, 24.2, 28.3$ ppt; $DO_{15} = 7.1, 10.2, 12.3, 9.7$ mg/L; $pH_{15} = 7.4, 7.5, 7.4, 7.5$, correspondingly) does not reveal any correlation either.

To investigate the influence of seawater chemical composition on the corrosion rates, several seawater samples were taken from the deployment site, and analyzed at the Wieland-Werke facilities. The results are summarized in Table 3.8. Concentrations of Ca,

Table 3.8. Seasonal variations in chemical composition of seawater at the deployment site measured at various depths. Top and bottom values represent measurements obtained at high and low tides, correspondingly. Coefficient of variation (CV) is calculated as ratio of standard deviation over the average of all measurements.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Aug-12 1m</th>
<th>Aug-12 2.3 m</th>
<th>March 2012 1m</th>
<th>March 2012 2.3 m</th>
<th>Oct. 2011 surface</th>
<th>Mean Value</th>
<th>CV(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca mg/l</td>
<td>378</td>
<td>414</td>
<td>298</td>
<td>304</td>
<td>349</td>
<td>342</td>
<td>13.2%</td>
<td></td>
</tr>
<tr>
<td>Cu mg/l</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.004</td>
<td>&lt;0.004</td>
<td>&lt;0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg mg/l</td>
<td>1,181</td>
<td>1,202</td>
<td>1,137</td>
<td>1,166</td>
<td>1,116</td>
<td>1,152</td>
<td>2.3%</td>
<td></td>
</tr>
<tr>
<td>Na mg/l</td>
<td>8,890</td>
<td>9,885</td>
<td>8,969</td>
<td>9,142</td>
<td>9,558</td>
<td>9,365</td>
<td>4.7%</td>
<td></td>
</tr>
<tr>
<td>pH at 23.2 ºC</td>
<td>7.6</td>
<td>7.7</td>
<td>7.9</td>
<td>7.9</td>
<td>7.8</td>
<td>7.77</td>
<td>1.6%</td>
<td></td>
</tr>
<tr>
<td>Conductivity µS/cm</td>
<td>48,100</td>
<td>47,500</td>
<td>46,000</td>
<td>47,400</td>
<td>46,800</td>
<td>47,078</td>
<td>2.1%</td>
<td></td>
</tr>
<tr>
<td>$K_{aq.1}$ mmol/l</td>
<td>2.15</td>
<td>2.17</td>
<td>2.03</td>
<td>2.06</td>
<td>2.45</td>
<td>2.13</td>
<td>8.3%</td>
<td></td>
</tr>
<tr>
<td>$K_{aq.2}$ mmol/l</td>
<td>0.25</td>
<td>0.21</td>
<td>0.14</td>
<td>0.15</td>
<td>0.16</td>
<td>0.18</td>
<td>27.7%</td>
<td></td>
</tr>
<tr>
<td>Carbonate hardness *d</td>
<td>6.0</td>
<td>6.1</td>
<td>5.7</td>
<td>5.8</td>
<td>6.8</td>
<td>5.97</td>
<td>6.0%</td>
<td></td>
</tr>
<tr>
<td>$\Sigma$ alkaline earth metals mmol/l</td>
<td>58.02</td>
<td>59.78</td>
<td>54.22</td>
<td>55.56</td>
<td>56.0</td>
<td>3.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total hardness *d</td>
<td>324.9</td>
<td>334.8</td>
<td>303.6</td>
<td>311.1</td>
<td>312</td>
<td>3.7%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Noncarbonate hardness *d</td>
<td>318.9</td>
<td>328.7</td>
<td>297.9</td>
<td>305.3</td>
<td>305</td>
<td>3.8%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloride mg/l</td>
<td>18,200</td>
<td>18,400</td>
<td>16,400</td>
<td>17,400</td>
<td>16,600</td>
<td>17,244</td>
<td>4.3%</td>
<td></td>
</tr>
<tr>
<td>Nitrate mg/l</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Orthophosphate mg/l</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfate mg/l</td>
<td>1,950</td>
<td>2,050</td>
<td>2,200</td>
<td>2,000</td>
<td>2,248</td>
<td>2,044</td>
<td>5.6%</td>
<td></td>
</tr>
</tbody>
</table>
Cu, Mg and Na were analyzed by induction-coupled plasma optical emission spectroscopy (ICP-OES) using Vista-MPX. The pH value was determined using a WTW pH 579 pH meter. The conductivity was measured using a WTW inoLAB Cond Level conductivity meter. Value of KS4.3 and KS8.2 were established by titration with hydrochloric acid and with sodium hydroxide solutions, correspondingly. Chloride, sulfate, orthophosphate and nitrate concentrations were measured by Photometry (MN Nanocolor) and by ion chromatography.

It can be seen from Table 3.8 that the seasonal variation of parameters is relatively small. Even though the low pH value, low carbonate hardness, and high sulfate content promote the corrosion of copper alloys, it is difficult to establish general trends for all of the tested materials. For example, high concentration of chloride lowers the probability of pitting corrosion in high-copper and copper-nickel alloys, but at the same time it increases the propensity to dezincification in brasses (see Sarver et al., 2010). However, variation of these chemical composition parameters does not appear to be large enough to account for the significant seasonal variations of corrosion rates presented in Fig. 3.7.

The level of stray electrical currents at the deployment site was evaluated using a custom-made monitoring system developed at the University of New Hampshire. The design and measurement procedure are presented in Drach and Tsukrov (2013) and Chapter 4. It consists of four Ag/AgCl electrodes positioned at 1 m distance in three directions. The data was continuously recorded at 200 Hz over the period of one month. It was found that the magnitude of both AC and DC currents (1 mV and 2 mV, correspondingly) was too small to affect the corrosion rates.

Overall, it appears that there is no correlation between the measured environmental factors at the site (physical and chemical) and the seasonal variations of the copper alloy corrosion rates during 3-month seawater exposure. Note, however, that the surface biofilms on the specimens were not analyzed in our study. As discussed in (Beech and Gaylarde, 1999), changes in microfouling can significantly influence the corrosion behavior of copper alloys.
3.4.4. Prediction of long-term corrosion rates based on the available corrosion data

An interesting question is whether the results of 3-month trials (if treated as independent tests) can be used to predict the longer-term corrosion rates. Assuming that dependence of material loss, \( \Delta m \), on the duration of exposure, \( t \), can be characterized by the parabolic law of Jones (1996)

\[
(\Delta m)^2 = C_m \cdot t,
\]

we can compare the observed one-year material loss with the value predicted by equation (3.4). Fig. 3.8 illustrates the material loss rate for Br-1. The coefficient \( C_m = 0.0256 \text{ g}^2 / \text{day} \) was calculated by linear regression of the four 3-month measurements. The difference between the actual and predicted one-year material loss in this case is \( \delta_{\text{year}} = 8.3\% \).

Table 3.9 presents the values of \( C_m \) and the corresponding differences for all considered alloys. The predictions of the model developed for CuNi-1 can be compared with the long-term corrosion data obtained by Efird and Anderson (1975) for specimens in the flowing seawater. The weight loss in Figure 1 of their paper corresponds to the corrosion rates of 6.9 \( \mu \text{m/year} \) after 7 years and 4.3 \( \mu \text{m/year} \) after 14 years. The model predicts the

![Graph showing material loss vs. time for Br-1](image-url)

**Fig. 3.8.** Material loss of Br-1 vs. time: blue diamonds represent measured data, and the black curve shows the corrosion behavior predicted by (3.4) based on four 3-month measurements.
corresponding rates of 5.5 \( \mu m/\text{year} \) and 3.9 \( \mu m/\text{year} \). These values are slightly lower than the reported data by Efird and Anderson (1975), which is consistent with the comparison of our measurements for 1 year exposure with their data (see Section 3.4.2).

However, it can be seen that for some materials (Br-4, CuNi-2, CuSi, Steel) the difference between the predicted and the actual values is more than 25%, which may suggest that the assumption of corrosion rate controlled by the parabolic law is not valid for these materials. Let us investigate whether the power law provides a more accurate description of changes in corrosion rate with time. We assume that the corrosion rate can be expressed as

\[
\alpha = C_a \cdot t^n
\]

where \( C_a \) and \( n \) are the material-specific parameters determined by data fitting based on all measurements for untensioned specimens in our study (four 3-month and one 12-month measurements). Fig. 3.9 provides examples of the obtained time-dependence curves for different types of the considered copper alloys (Br-4, CuNi-2, CuSi, and Cu). Parameters \( C_a \) and \( n \) for all investigated materials are presented in Table 3.9. The last column presents values of correlation coefficient for the power law fit:

\[
R^2 = 1 - \frac{\sum (\log \alpha_i - \log \bar{\alpha})^2}{\sum (\log \hat{\alpha}_i - \log \alpha_i)^2}
\]

### Table 3.9. Model parameters for parabolic and power law material loss models.

<table>
<thead>
<tr>
<th>Material</th>
<th>( C_m \cdot g^2/\text{day} )</th>
<th>( \delta_{\text{1 year}, %} ) ( \delta )</th>
<th>( C_a, \mu m \cdot \text{year}^{-n} )</th>
<th>( n )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>0.0256</td>
<td>8.3</td>
<td>16.5</td>
<td>0.61</td>
<td>0.89</td>
</tr>
<tr>
<td>Br-2</td>
<td>0.0284</td>
<td>14</td>
<td>16.7</td>
<td>0.63</td>
<td>0.95</td>
</tr>
<tr>
<td>Br-3</td>
<td>0.0316</td>
<td>25</td>
<td>17.3</td>
<td>0.63</td>
<td>0.97</td>
</tr>
<tr>
<td>Br-4</td>
<td>0.0107</td>
<td>226</td>
<td>3.50</td>
<td>1.41</td>
<td>0.94</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>0.0166</td>
<td>6.1</td>
<td>13.2</td>
<td>0.54</td>
<td>0.59</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>0.1009</td>
<td>34</td>
<td>27.5</td>
<td>0.70</td>
<td>0.97</td>
</tr>
<tr>
<td>CuSi</td>
<td>0.0233</td>
<td>26</td>
<td>13.8</td>
<td>0.67</td>
<td>0.93</td>
</tr>
<tr>
<td>CuTin</td>
<td>0.0116</td>
<td>7.2</td>
<td>10.5</td>
<td>0.59</td>
<td>0.76</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0188</td>
<td>13</td>
<td>13.5</td>
<td>0.61</td>
<td>0.95</td>
</tr>
<tr>
<td>Steel</td>
<td>0.6991</td>
<td>-33</td>
<td>175</td>
<td>0.05</td>
<td>0.01</td>
</tr>
</tbody>
</table>

\[ \delta_{\text{1 year}} = \frac{\Delta m_{\text{predicted}} - \Delta m_{\text{actual}}}{\Delta m_{\text{actual}}} \cdot 100\% \]
where $\alpha_i$ is the corrosion rate measurement, $\bar{\alpha}$ is the average of all corrosion measurements for a given material, $\hat{\alpha}_i$ is the predicted value for each data point. The better the fit quality, the higher is the value of $R^2$. As can be seen, for most of the alloys, this data can be considered to provide good estimates of long-term corrosion behavior.

According to (3.5), the deceleration of corrosion rate with time is quantified by exponent $n$. We observe that its value is approximately 0.6 for all considered brasses (except Br-4), pure copper $Cu$ and tin bronze $CuTin$. For $CuNi-2$ and $CuSi$, the value of $n$ is approximately 0.7, which indicates increased deceleration of corrosion for these two alloys. For $CuNi-1$ and $Steel$ the power law appears to be a poor model with correlation coefficient $R^2$ equal to 0.6.

![Graphs showing power law material loss models for various metals](image)

**Fig. 3.9.** Plots of power law material loss models for Br-4, CuNi-2, CuSi, and Cu: blue diamonds represent measured data, and black curves represent modeled behavior using (3.5).
and 0.01, correspondingly. Note that the obtained values of the power law exponent for CuNi-1 and bronzes are in good correlation with previously published results of Mansfeld et al. (1992): they observed the range of 0.6 - 0.8 for CuNi-1 and the value of 0.6 for bronzes. However, our estimate for brass ($n = 0.6$) is slightly higher than that of Mansfeld et al. (1992) ($n = 0.5$).

3.5. Biofouling resistance studies

The results of the biofouling study are summarized in Fig. 3.10 (right bars for each material). They are based on the analysis of three sets of copper alloy plates and nylon net panels processed immediately after the recovery. The analysis procedure is described in Greene and Grizzle (2007), Drach et al. (2013). As can be seen, most alloys had no biofouling organisms at the end of the deployment period, indicating 100% inhibition of biofouling. Alloys CuNi-1 and CuTin had minimal growth with only one taxon at Phylum level (P. Mollusca) present. Such a good biofouling inhibition of copper alloys was expected based on the previous studies (Efird, 1975; Michel et al., 2011). In contrast, alloy Br-4 had five taxa

Fig. 3.10. Corrosion and biofouling data for continuous 12-month exposure: blue bars represent uniform corrosion rates in μm/year; diagonally filled bars with the corresponding numeric values represent biofouling accumulation data in g.
(Echinodermata, Mollusca, Chordata, Arthropoda, Annelida) totaling 267 g biomass on three plates. The nylon netting specimens accumulated six taxa (the same phyla as on Br-4 plus Porifera) totaling 668 g on three panels. Although it is not possible to directly compare performance of the nylon netting and copper alloy plates due to the differences in surface area and shape, the data strongly indicates higher biofouling resistance of all tested copper alloys with the exception of Br-4.

There are two possible phenomena that can be responsible for the reduced biofouling resistance of Br-4. One is the lower copper ion release rate (due to the lower corrosion rate) as compared to other tested alloys, see Table 3.7. The lower release rate results in a lower concentration of biocidal cupric ions (Cu²⁺, see Borkow and Gabbay, 2005; Santo et al., 2008) on the surface, thus inhibiting biofouling resistance (Michel et al., 2011). Another possible reason can be the preference of the fouling organisms to a specific composition element present in the alloy (this alloy is the only one that contains Aluminum). The published data on nickel aluminum bronzes (e.g. CuAl9Ni5Fe4, see Francis, 2010) shows that these alloys are prone to biofouling (Wang, 2009) even at a significantly higher corrosion rate than Br-4 (25-50 vs. 4 μm/year). This suggests that the adhesion preferences of barnacles to Aluminum could be the major reason for low biofouling resistance of Br-4. This hypothesis is also indirectly supported by the comparison of surface condition of tensioned Br-4 and untensioned CuTin specimens. Both of them exhibit the same corrosion rate (10-11 μm/year), however there is no barnacle population on CuTin, see Fig. 3.11. Observations from our study are consistent with those of Bulow (1945) who observed that additions of Aluminum to pure copper, silicon bronze and 75/25 brass significantly inhibited their biofouling resistance.

Although the present study documents the biofouling resistance properties, it does not provide information on the duration of such properties. It appears that longer-term studies are needed (Efird, 1975) to reveal differential responses among the taxa and the reduction in biofouling resistance over longer periods of exposure (more than 18 months). It is also interesting to note that with the exception of one alloy (Br-4), all tested copper alloys showed good biofouling resistance with corrosion rates as low as 10 μm/year which is almost two times lower than the guidelines (18 μm/year) provided in Francis (2010).
3.6. Localized corrosion studies

3.6.1. Light-optical microscopy of cross-sections

The microscopic images of cross-sections of all recovered samples were analyzed to determine the localized corrosion penetration as illustrated in Fig. 3.12. The microscopy was performed at Wieland-Werke (Germany). The specimens were prepared following the procedure described in Hofmann et al. (2005). It is important to note that no dealloying, distinct intercrystalline cracks or stress corrosion cracking were observed in the cross-sections. For most alloys, only very small grooves at grain boundaries or very small pits were found. The absence of dezincification was somewhat unexpected given the high chloride concentration of seawater (see Table 3.8). Brasses Br-1, Br-2, Br-3 are expected to have resistance to dezincification due to their alloying additions of P, Sb and Sn as suggested by Davies (1993). However, for the Br-4 alloy there is no obvious explanation for its good performance observed in the field test, because this alloy exhibited high level of dezincification in the standard lab test (see Table 3.4).
Table 3.10. Localized corrosion rates in $\mu$m/year.

<table>
<thead>
<tr>
<th>Material</th>
<th>12-month</th>
<th>12-month</th>
<th>Relative difference*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>untensioned</td>
<td>tensioned</td>
<td></td>
</tr>
<tr>
<td>Br-1</td>
<td>29</td>
<td>18</td>
<td>58%</td>
</tr>
<tr>
<td>Br-2</td>
<td>19</td>
<td>21</td>
<td>-12%</td>
</tr>
<tr>
<td>Br-3</td>
<td>21</td>
<td>15</td>
<td>37%</td>
</tr>
<tr>
<td>Br-4</td>
<td>18</td>
<td>24</td>
<td>-27%</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>23</td>
<td>24</td>
<td>-6%</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>22</td>
<td>22</td>
<td>0%</td>
</tr>
<tr>
<td>CuSi</td>
<td>29</td>
<td>21</td>
<td>38%</td>
</tr>
<tr>
<td>CuTln</td>
<td>15</td>
<td>12</td>
<td>25%</td>
</tr>
<tr>
<td>Cu</td>
<td>17</td>
<td>14</td>
<td>18%</td>
</tr>
</tbody>
</table>

* $\delta = \frac{\alpha_{\text{tensioned}} - \alpha_{\text{untensioned}}}{\alpha_{\text{untensioned}}} \times 100%$

Fig. 3.12. A light-optical micrograph of a cleaned cross-section of (a) Br-3 and (b) Br-4 after 12 month exposure in untensioned configuration.

A summary of the localized corrosion measurements is presented in Table 3.10. The localized corrosion was calculated as the average of two largest pit depths observed on the opposite face of the specimen. It can be seen that for most alloys there is no significant difference in the localized corrosion between the tensioned and untensioned testing configurations. The largest differences are observed for Br-1 (58%), Br-3 (37%) and CuSi (38%) with untensioned specimens experiencing higher level of localized corrosion attacks.

3.6.2. Scanning-electron microscopy and X-ray spectroscopy of surface condition

The corroded surfaces of the samples were characterized by scanning electron microscopy (SEM). Images were created before and after removal of the layers of corrosion products formed on the samples during the seawater exposure. Two samples with
dimensions of 10 x 10 \text{mm}^2 were prepared from all sheets. One of the two samples of each alloy was treated with citric acid to remove the layer of corrosion products, and the other one was analyzed untreated. For each of the samples, secondary-electron images were created and analyzed at magnifications of 100x up to 2,000x.

The SEM images (Fig. 3.13a,c) show that in most cases the alloys are covered with the tight oxide layers containing a network of cracks. It is suspected that these cracks formed due to the handling of the samples in air environment for SEM imaging. The images obtained after the removal of corrosion layers (Fig. 3.13b,d) reveal the interfaces between the base metal and the corrosion layer. For most of the tested alloys, the observed surface structure seems to be related to the grain structure.

Fig. 3.13. SEM images (secondary electrons) of the surfaces of samples of Br-3: (a) untensioned with corrosion layer; (b) untensioned without corrosion layer; (c) tensioned with corrosion layer; (d) tensioned without corrosion layer.
It is interesting to compare the surface corrosion patterns of CuNi-1 and CuNi-2 (Fig. 3.14). While CuNi-2 exhibits mostly intergranular grooves, the surface of CuNi-1 contains distinct small pits. These pits can be related to the presence of Fe and Ni rich particles.

The chemical compositions of the corrosion layers were determined simultaneously with SEM analysis using energy-dispersive X-ray (EDX) spectroscopy. The data was obtained at magnification factor of 500x which corresponds to the 220 x 155 μm² area of interest. The EDX was performed with an accelerating voltage of 10 – 20 kV which corresponds to the penetration depth of approximately 1 μm. This depth is relatively shallow compared to the thickness of observed corrosion layers. The results were used to determine changes in relative content of alloying elements in the corrosion layer as compared to the base material. The content of each element was normalized by the total percentage content of all alloying elements. “Relative difference”, Δril, in composition was calculated by subtracting this “relative content” in the sample with the intact corrosion layer from the relative content of the sample without the protective layer:

\[
\Delta r_i = r_i^{\text{layer}} - r_i^{\text{base}} = \frac{x_i^{\text{layer}}}{\sum x_i^{\text{layer}}} - \frac{x_i^{\text{base}}}{\sum x_i^{\text{base}}}
\]

where \( x_i^{\text{layer}} \) and \( x_i^{\text{base}} \) are the content of the alloying element \( i \) obtained from EDX analysis.

Fig. 3.14. SEM images of the cleaned surfaces without corrosion layer of (a) tensioned CuNi-1 and (b) untensioned CuNi-2.
of the sample with corrosion layer (layer) and without it (base), correspondingly; \( \sum_i^n x_i^{layer} \) and \( \sum_i^n x_i^{base} \) are the sum of the contents of all alloy constituents of the sample with corrosion layer (layer) and without it (base). A positive value for the relative difference means that the alloying element \( t \) is enriched in the corrosion layer, whereas a negative value indicates that the corrosion layer is depleted with respect to this element. Note that because EDX does not provide information on the chemical states of the species and hydrogen content, the exact chemical composition of the corrosion layer (including the organic compounds and poly-atomic anions) cannot not be determined. However, this approach allows to determine the alloying elements which were preferentially incorporated into the corrosion layer, thus promoting or dominating the layer formation. During the data processing, only the elements present in the initial composition were considered.

The relative composition of alloying elements in the base material and in the corrosion layers is presented in Fig. 3.15 and Tables 3.11 and 3.12. It can be seen that the corrosion layer in the brasses \( Br-1, Br-2 \) and \( Br-3 \) is characterized by the increased levels of Tin and Copper, and decreased levels of Zinc. Depletion of Zinc is expected due to the formation of

| Table 3.11. Major enriched and depleted alloying elements in the corrosion layer from untensioned testing setup. |
|---|---|---|---|---|---|---|---|
| Br-1 | Br-2 | Br-3 | Br-4 | CuNi-1 | CuNi-2 | CuSi | CuTin |
| Enriched (%) | 12.0 Cu 13 Sn | 10.8 Cu 0.4 Sn | 0.2 Cu 6.9 Sn | 22.2 Zn 10.8 Al | 16.5 Ni 3.1 Fe 1.2 Mn | 14.6 Cu 0.3 Cu 0.8 Sn 3.3 Sn |
| Depleted (%) | 12.9 Zn 0.4 Ni | 11.6 Zn 7.0 Zn | 33.1 Cu 20.8 Cu | 9.2 Ni 5.2 Zn 0.9 Mn 3.3 Cu |

| Table 3.12. Major enriched and depleted alloying elements in the corrosion layer from tensioned testing setup. |
|---|---|---|---|---|---|---|---|
| Br-1 | Br-2 | Br-3 | Br-4 | CuNi-1 | CuNi-2 | CuSi | CuTin |
| Enriched (%) | 9.1 Cu 6.1 Sn | 1.6 Cu 5.4 Sn | 0.2 Cu 6.0 Sn | 29.4 Zn 12.0 Al | 17.3 Ni 18.6 Fe 0.3 Mn | 13.3 Cu 4.4 Si 14.6 Sn |
| Depleted (%) | 14.8 Zn 0.4 Ni | 5.6 Zn 6.2 Zn | 41.4 Cu 36.1 Cu | 9.7 Ni 3.3 Zn 3.7 Cu 0.3 Mn 0.7 Mn 14.6 Cu |
soluble chloride compounds, and enrichment of Tin is attributed to the formation of insoluble Tin oxides (Francis, 2010). In this way, Tin promotes the formation of protective layer, while Zinc is preferentially corroded away. The same effect of Tin is observed in CuTin.

Alloy Br-4 exhibits a rather different behavior than other brasses in this study: the copper in the corrosion layer is significantly depleted while Zinc and Aluminum are retained. Due to the presence of Aluminum in the alloy, the corrosion produces a thin film made up of

![Graph](image-url)

**Fig. 3.15.** Relative composition of alloying elements in the base material (left stacks) and the corrosion layer (right stacks). The data was obtained by EDX for the samples from (a) untensioned and (b) tensioned testing configurations.
Aluminum oxides and elements taken up from seawater (see discussion of hydrotalcite films in Francis, 2010). This mechanism is different from the other investigated brass alloys, in which a thick layer is formed from the oxides of alloying elements. It is also possible that the effects related to biofouling contributed to the increased release of copper (and relative enrichment of Aluminum) from the corrosion layer in Br-4.

The low corrosion performance of CuNi-2 (see Tables 3.7 and 3.10) can be related to the observed composition of its corrosion layer. In contrast to CuNi-1, this alloy exhibits significant loss of the passivating elements (Nickel and Zinc) in both tensioned and untensioned testing configurations. Therefore, no alloying element appears to contribute to the protective layer formation.

The data for CuNi-1 and CuSi shows different performance in tensioned and untensioned configurations. The corrosion layer of CuNi-1 in the tensioned configuration is characterized by the significantly higher degree of iron enrichment resulting in the increased depletion of copper. However, in both configurations we observed enrichment of iron and nickel, which is consistent with the previously reported data in Efird (1977). For CuSi, the tensioned configuration specimen shows increased levels of Silicon in the corrosion layer as compared to the untensioned specimen.

3.7. Major observations from the corrosion study

A one-year field testing of corrosion performance of copper alloys in natural seawater was carried out in the North Atlantic Ocean. The data from this study allowed to capture seasonal variations in corrosion behavior and compare the performance of tested alloys during 3-month and 12-month exposure periods (the results are summarized in Table 3.7). Light optical microscopy and SEM/EDX analyses were performed to investigate and quantify the localized corrosion damage, and estimate which alloying elements promote the corrosion layer formation. For all of the tested materials no dealloying or intergranular attacks were observed. The maximum corrosion penetration depths are summarized in Table 3.10.
Overall, the tested alloys showed similar corrosion and biofouling performance with the exception of Br-4 and CuNi-2. Alloy CuNi-2 exhibited relatively high uniform corrosion rate compared to the other tested alloys. Corrosion resistance of Br-4 was better than those of the rest of the tested alloys, however, this alloy exhibited poor biofouling resistance. It is not clear if its poor biofouling performance is caused by the low corrosion rate. It appears that the presence of Aluminum could account for the inhibited biofouling resistance of this particular alloy. The biofouling resistance of other alloys was found to be excellent over the 12-month exposure period.

The major observations are summarized as follows:

- Corrosion rates of copper alloys after 3-month exposure are approximately 2.4 higher than after 12-month.
- Corrosion rates after 12-month exposure under tensile time varying load are on average 39% higher than those in the untensioned fixed configuration.
- There is no direct correlation between the physical/chemical environmental parameters and the variations in the seasonal corrosion rates. However, microfouling was not studied, and it is suggested that analysis of microfouling can provide insight into this phenomenon.
- Good biofouling resistance is demonstrated by practically all investigated copper alloys with corrosion rates as low as 10 $\mu$m/year. The only exception is Br-4 characterized by the low copper ion release rate (corrosion rate) and the presence of Aluminum in its composition.
- Presence of tin in the composition of Br-1, Br-2, Br-3, CuTin reduces their corrosion rate as shown by EDX studies.
- Corrosion layer of Br-4 is depleted of copper which is a significantly different behavior compared to the other tested brasses. This could be related to biofouling.
- Relatively high corrosion rate of CuNi-2 could be explained by its unusual corrosion layer composition: copper is substantially depleted.
- Localized corrosion penetration of the specimens in tensioned configuration is on average 8% lower than that of specimens tested in the untensioned fixed setup. This is in contrast to the higher uniform corrosion rates of the tensioned specimens.
Chapter 4. Low Cost Real-Time Stray Current Monitoring System for Seawater Field Studies

This chapter describes a low cost three-axis stray electric current monitoring device designed for field deployments. The system consists of a remotely operated PC with a set of pseudo-electrodes and a digital compass. The collected data is analyzed to determine magnitudes of AC and DC components of electric field and dominant AC frequencies. Using simplified analysis, this information is processed to estimate the maximum potential effect of the observed stray currents on the collected corrosion data in the same location. It is shown that DC currents should not affect the observed corrosion rates by more than 25%, and that effect of AC currents can be considered negligible. Based on the experience gained in testing of the proposed design, some suggestions for improving the robustness, reducing costs and power supply requirements are proposed.

4.1. Review of the available stray current monitoring devices

Presence of electric stray currents in the corrosive environment adversely affects the corrosion behavior of structures by amplifying the material loss rates (Lennox and Peterson, 1974; Hack and Wheatfall, 1995). In industrial applications, this phenomenon leads to increased expenditures on corrosion protection and premature failure of components. In research, this phenomenon may invalidate the collected testing data. Therefore, it is important to have accessible tools for detection and monitoring of stray currents for field testing of corrosion rates.

Stray current monitoring devices (SCMD) can be classified by their mobility (portable or stationary), by their recording capability (instantaneous measurements or data recording), and the ability to measure the direction of stray currents (single or multi-axis). The basic design of a single-axis portable SCMD (Campbell, 1981) consists of a pair of Ag/AgCl reference electrodes attached to a hand-held voltmeter. With only one axis, the measurements are taken by manually rotating the device in horizontal plane and recording the observed DC voltage. However, in this case the vertical component of the electric field is not analyzed.
A more sophisticated single-axis SCMD is discussed in Webb et al. (1985). In this design, the authors focused on obtaining very high sensitivity ($10^{-12} \text{ V/m}$) for low frequency signals (up to 60 Hz). The measurements were obtained by using Ag/AgCl reference electrodes at a distance of 200 – 1000 m attached to an intricate electronic system with high-gain amplifiers and a recording device. While it is a very robust design allowing deep sea deployments, this device is not well suited for monitoring stray currents with respect to corrosion processes. The limitations for this application include limited sensing range (very low voltages), large dimensions (low spatial resolution), and lack of information on all three components of the electric field.

A multi-axis portable SCMD design, consisting of hand-held gun with an array of four pseudo-reference electrodes is described by Jenkins (2001). In comparison to single-axis units, this device provides information about the electric field gradients in a single measurement, and allows for detection of both AC and DC stray currents. Data recording is also possible by attaching the device to a data logger on the support vessel. However, due to its portability the arrangement of electrodes was constrained to a 7.5 cm tube, which limits the sensitivity to 3 mV/m.

In this paper, the authors propose a design of a low cost multi-axis SCMD for field studies in natural seawater. The proposed design allows for identification, remote monitoring, and recording of AC/DC currents with adjustable range (from ±0.02 V/m up to ±10 V/m) and bandwidth (up to 1 kHz). The prototype was manufactured and deployed for a total of 30 days at the location of field testing of copper alloys at Portsmouth Harbor (see Chapter 3). The collected data was analyzed to determine the magnitude of AC and DC currents and the dominant frequencies of AC currents. The data was processed to estimate the effect of observed electric currents on the corrosion rates of copper alloys.

4.2. Design of the proposed system

Based on the short survey of published literature on SCMD designs, it was decided that none of the published designs meet the requirements for sensitivity and resolution needed in monitoring stray electric currents during the field trials in natural seawater. Most of the
available commercial solutions are not only very expensive but also designed for monitoring cathodic protection systems. Therefore, their design was not directly applicable for this application and required modifications to integrate into the monitoring system and adapt sensing range and bandwidth.

The proposed design is a low cost stationary three-axis SCMD with remote real-time monitoring and flexible data acquisition capabilities. This configuration allows one to: (1) install the SCMD for the full time of the field trials; (2) obtain complete information on the magnitude, frequency and direction of stray currents; (3) allow for remote monitoring and data processing; and (4) remotely adjust range and bandwidth based on the observed data.

The first step in the design of SCMD was to choose an appropriate sensor for electric field detection. Two types of electrodes are typically used in seawater applications: Ag/AgCl reference electrodes and dry Ag/AgCl pseudo-reference electrodes (Ansuini and Dimond, 1994; APL, 2001; Zhang, 2011). Even though reference electrodes provide higher stability and lower noise level (Bott, 1995), their design requires clean deployment environment due to the use of porous membrane as a junction. Biofouling in harbors or shallow deployment locations may quickly contaminate the junction and disable the electrode. Since the deployment location is known to experience heavy fouling during the summer months (Drach et al., 2012a), dry type pseudo-reference electrodes were chosen. In addition to higher resilience to biofouling (Park, 2007), this type of electrode has lower impedance (Bott, 1995; Zhang et al., 2009) and cost.

The next step was to determine the required spatial resolution of SCMD, number of sensors, and their arrangement. For this design, the dimensions (1 x 1 x 1 m³) were chosen to be similar to the scale of the testing frame for holding corrosion specimens (see Chapter 3). Note that larger separation between the electrodes would increase the amplitude sensitivity, but, at the same time, decrease the spatial resolution due to inability to resolve field features between the electrodes. With respect to the arrangement, it was chosen as an orthogonal triad, so that field gradient is easily calculated in 3D Cartesian coordinates.
Fig. 4.1 illustrates the prototype of the proposed design. Dry Ag/AgCl electrodes (enclosed into blue PVC housings with red caps) are attached to the frame with dimensions of $1 \times 1 \times 1 \text{ m}^3$ made of $\frac{3}{4}$ in. (20 mm) PVC pipes. Following the orthogonal triad arrangement, the center electrode is denoted as Electrode 0, with other electrodes denoted as X, Y, Z. The separation distances between 0 and X, Y, Z are 1.15, 1.0, 0.91 m, respectively. Each electrode is an off-the-shelf preassembled sensor with 15 m of stranded copper wire (RHH #14 AWG).

Since the frame is designed for deployment from the floating platform in moving water, a digital compass (2-axis magnetometer) was added to the system to allow for compensation of rotations in the horizontal plane. According to the manufacturer's specifications, this module is not capable of tilt compensation, and therefore it is highly sensitive to tilting (2 degrees of error in orientation per each degree of tilt). To ensure horizontal orientation, the compass module was sealed into the PVC elbow pipe case and securely attached to the frame along the X-axis. In this configuration, the compass records the azimuth orientation of X-axis with respect to magnetic North.
Wiring for compass and electrodes is lined along the frame and loosely attached to the pre-tensioned rope to provide stress relief during the deployment. All wires are connected to the control system (see Fig. 4.2) consisting of a mini PC with data acquisition (DAQ) and digital interface USB boards. All components are off-the-shelf commercial products. The PC is a standard x86-based computer operated by Windows OS with Wi-Fi connectivity. User interface is provided using the remote desktop feature of the OS, which allows to control the computer locally on site with a smartphone or a tablet, or remotely from a workstation over the Internet.

DAQ board has eight differential (16 single-ended) analog input channels with ±10 V range and adjustable input gain (1, 10, 100, 500). It is capable of acquiring data with 16-bit resolution at a frequency up to 2 kHz per channel. Electrodes are connected in the pseudo-differential configuration with Electrode 0 wired as a common ground, and Electrodes X, Y, Z wired to channels 0, 1, and 2, respectively. All channels are assigned a maximum gain of 500 (range of ±0.02 V). Data acquisition frequency is chosen as 200 Hz with expectation that dominating frequency of AC stray currents is 60 Hz or lower.

Digital interface board is capable of communication over PC interface with digital sensors such as the digital compass used in the prototype system. Since this interface was
originally developed for chip-to-chip communication, it is limited to short length of cables (under 1 m) at a standard clock speed (100 kHz). To overcome this limitation and increase the range to 15 m, the following modifications were made:

- high-quality shielded twisted pair cable was used for wiring (Cat 6), with data and clock lines separated into different pairs;
- clock speed was reduced to 50 kHz (communication was possible up to 70 kHz but lower value was chosen for stability).

The compass module is an integrated system with a microprocessor capable of self-calibration, calculation of heading (based on internal readings from magnetometers) and averaging. It was set to continuous measurement mode with DAQ frequency of 10 Hz and averaging window of 10 (every reported data point is an average of 10 measurements).

A software tool with graphical user interface (see Fig. 4.3a) was developed to provide control of the DAQ board parameters, real-time monitoring and data logging. This tool allows configuration of the input channels and set the DAQ frequency. It has two plotting functions: virtual scope and time history plot. A similar tool (see Fig. 4.3b) was developed for control, monitoring and data logging of compass data. Its purpose is to configure operation mode and parameters of compass module, set the DAQ frequency. It provides two visualization options: virtual compass and time history plot.

![Fig. 4.3. Graphical user interface for (a) DAQ system, (b) digital compass.](image-url)
4.3. Laboratory testing of the prototype

Prior to deployment, the system was tested in the lab to ensure that: (1) the electrodes are stable and have minimal DC offset relative to Electrode 0; (2) the electrodes are capable to accurately capture electric field in seawater; (3) hardware is compatible (4) communication between components is stable; (5) the developed software does not contain any obvious bugs; (6) remote operation is reliable.

In the first test, the electrodes were submersed into a plastic tub with 5 gallons (18.9 L) of natural seawater for a total of twelve hours (Fig. 4.4). The system was remotely operated via a workstation to turn on the data recording and real-time monitoring. However, data recording automatically stopped after about 6 hours. It was determined that the visual plots required too many resources from the mini PC (old 2002 CPU with low computational power), and therefore they were disabled. Numeric real-time indicators were added in their place. The recorded data showed that after about an hour all electrodes reached a steady state and the DC offsets with respect to Electrode 0 were documented as +0.25 mV, −0.28 mV and −0.31 mV for X, Y, and Z, respectively. Spectral analysis of the recorded steady state signal revealed flat noise floor in the range 0.01 – 100 Hz, which corresponds to the sensitivity of 0.01 mV. Compass data was steady without any numerical noise. This was attributed to the internal averaging algorithm and 0.1° output resolution of the compass module.

Fig. 4.4. Lab testing of the electrodes.
In the second test, the electrodes were subjected to a constant field gradient of AC electric current in the same environment (plastic tub with natural seawater). It was achieved by submersing two rectangular plates separated by 0.5 m and attached to a signal generator that produced constant amplitude sinusoidal signal (Fig. 4.5). The test was performed for several amplitudes (20 – 50 mV/m) and several frequencies (10 – 60 Hz) with electrodes located very close to the surface of the plates. The analysis showed good accuracy in capturing signal in this configuration (96 – 98% depending on the accuracy of positioning). Additionally, the electrodes were moved away from the plates and tested at distances of 0.2 m and 0.23 m subjected to the AC field at 20 Hz with amplitude of 20 mV/m. The recorded data reproduced the expected voltage (4 mV and 4.6 mV, respectively) with accuracy of 95 – 96%. The observed difference was attributed to the error in the measurements of electrode position and to the slight non-uniformity of the electric field due to geometrical constraints.

4.4. Field deployment of the prototype

The prototype of the proposed 3-axis SCMD design was deployed at Portsmouth Harbor (New Hampshire, USA) in the North Atlantic Ocean over the period of 30 days (05/20/12 – 06/20/12). It was used to collect information on stray electric currents for the location of
corrosion testing of copper alloys. Therefore, the system was installed in close proximity to copper alloy specimens. It was suspended from the floating platform at 1 m depth from the water surface.

The location has an average water depth of 5.1 m with tidal variations of ±1.5 m. Environmental conditions are monitored by a set of sensors which provide information on temperature, salinity, dissolved oxygen and pH levels. The average values during the deployment period were 12.7°C, 27.9 ppt, 9.5 mg/L and 7.5, respectively.

In the first week of the deployment, it was determined that the system was unable to sustain continuous recording of data from DAQ board for longer than 8 hours. The cause was identified as insufficient CPU power. This issue was addressed by optimizing the data logging procedure and remotely updating the software. Over the course of the deployment, the system was routinely checked (over the Internet) for abnormal measurements, range of recorded values and electric drift of electrodes.

Upon the recovery, the system was inspected for damage and component failure. No structural damage or electrical failures were observed. However, heavy fouling was documented (see Fig. 4.6). This was expected based on the previous experience with

Fig. 4.6. Fouling of the system after 30-day deployment in North Atlantic.
deployments at the same location during the summer months (Drach et al., 2012a). After pressure-wash cleaning of the frame and electrode housings, the electrodes were inspected for any changes in the surface condition of AgCl film. Surface of all electrodes was intact without visible changes in color/roughness. The electrodes were also checked for stability and changes in DC offset using the same setup as in the initial testing. No significant changes were observed.

4.5. Collected stray current data processing and results

The collected data was processed to determine the changes in DC electric field strength, and evaluate dominant AC frequencies with the corresponding amplitudes throughout the deployment period. Table 4.1 presents the summary on the recorded data over nine time intervals varying in duration from 7.6 to 235 hours. It provides basic statistics of the electric field magnitude (mean and 99.95% percentile values calculated based on the X, Y, Z measurements), and azimuth orientation of the X-axis (min/mean/max values from compass measurements). Fig. 4.7 illustrates the recorded data for data segment #8 with raw measurements shown in blue and 1-minute averages shown in black.

Table 4.1. Summary of the recorded data segments. Gap represents the duration of the periods when recording system was not active. Orientation is given with respect to the magnetic North.

<table>
<thead>
<tr>
<th>#</th>
<th>Start</th>
<th>End</th>
<th>Duration, h:mm:ss</th>
<th>Gap, h:mm</th>
<th>Observations, millions</th>
<th>Magnitude, mV/m</th>
<th>X-axis Orientation, °</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5/20 16:00:48</td>
<td>5/20 23:39:31</td>
<td>07:38:43</td>
<td></td>
<td>5.5</td>
<td>1.71</td>
<td>246.8 267.0 252.3</td>
</tr>
<tr>
<td>2</td>
<td>5/22 04:04:40</td>
<td>5/22 12:05:36</td>
<td>08:00:56</td>
<td>28:25</td>
<td>5.8</td>
<td>1.38</td>
<td>243.3 259.9 249.5</td>
</tr>
<tr>
<td>3</td>
<td>5/22 15:52:51</td>
<td>5/22 23:54:39</td>
<td>08:01:48</td>
<td>03:47</td>
<td>5.8</td>
<td>1.14</td>
<td>246.1 264.0 251.1</td>
</tr>
<tr>
<td>4</td>
<td>5/23 00:04:09</td>
<td>5/23 08:11:09</td>
<td>08:07:00</td>
<td>00:09</td>
<td>5.8</td>
<td>1.04</td>
<td>243.7 265.5 254.4</td>
</tr>
<tr>
<td>5</td>
<td>5/23 17:24:07</td>
<td>5/24 01:23:06</td>
<td>07:58:59</td>
<td>09:12</td>
<td>5.8</td>
<td>0.96</td>
<td>247.1 263.2 252.7</td>
</tr>
<tr>
<td>6</td>
<td>5/24 06:02:35</td>
<td>5/27 01:00:33</td>
<td>06:57:58</td>
<td>04:39</td>
<td>48</td>
<td>1.12</td>
<td>243.1 266.4 252.5</td>
</tr>
<tr>
<td>7</td>
<td>5/27 17:16:42</td>
<td>6/03 01:01:09</td>
<td>151:44:27</td>
<td>16:16</td>
<td>109</td>
<td>2.00</td>
<td>244.5 288.0 254.9</td>
</tr>
<tr>
<td>8</td>
<td>6/05 20:21:45</td>
<td>6/10 01:01:09</td>
<td>100:39:24</td>
<td>67:20</td>
<td>73</td>
<td>1.74</td>
<td>243.5 278.0 259.9</td>
</tr>
</tbody>
</table>
Fig. 4.7. Example of the recorded data: raw measurements are shown in blue, 1-minute averages are shown in black.
To characterize the changes in DC electric field strength, the following steps were performed:

1) collected data on X,Y,Z components was used to calculate the magnitude of electric field gradient.
2) each data segment was analyzed to determine min, max, mean, 0.05% and 99.95% percentile values for the recorded characteristics of electric field. These statistics provide information not only on the single instantaneous spikes but also on the “effective” min (0.05%) and max (99.95%) values observed.
3) plots of raw data and 1-minute averages (as shown in Fig. 4.7) were visually inspected for any trends or instantaneous changes which cannot be captured by the descriptive statistics.
4) the variations in the summary statistics between the data segments were analyzed.

The analysis revealed that variations in mean values for all components of electric field and its total magnitude were within the range of ±2 mV. The maximum value of 2.0 mV for field strength (caused by the increase in mean value for X component) was observed in the data segment #7. A total of 7 instantaneous spikes (1 in X, 2 in Y, and 4 in Z) over the 20 mV range were observed out of 428 million observations per channel. These instances were analyzed and determined to be single data points without any surrounding points at elevated levels. It was concluded that these measurements were caused by some malfunctions in the DAQ system. The overall minimum for 0.05% and overall maximum for 99.95% percentiles were determined to be -3.9 – 3.5 mV for individual components and 0.1 – 4.6 mV for the total magnitude.

Compass data was analyzed following the same procedure. It was determined that mean orientation of X-axis was 257° with respect to magnetic North with variations of ±20° corresponding to tidal periods. The instantaneous min and max values were 243° and 288°, respectively.

AC component of the electric field was characterized by analyzing one-sided power spectral densities (PSD) for the components and the magnitude of electric field. PSDs were calculated using discrete Fourier transform after detrending the data (by subtracting the
mean value). An example of the calculated PSDs is shown in Fig. 4.8 with raw spectra shown in red and 100-band averages shown in black. The plots also include the band-averaged spectra from lab testing of electrode stability shown in blue.

Fig. 4.8. Power Spectral Density (PSD) plots for data presented in Fig. 4.7. Raw spectra are shown in red; 100-band averages are shown in black; 100-band averaged spectra from lab testing are shown in blue.
The dominant frequency for all data segments was calculated to be 60 Hz, confirming the initial hypothesis that the stray AC currents may be present due to leaks from powered boats in the area. The total maximum amplitude of AC signal was under 1 mV, with most of the energy attributed to 60 Hz frequency. The spectra also exhibited spikes of lower magnitude at 20 Hz and 100 Hz for X, Y, Z components, and at 10, 20, 30, 40, 50, 70, 80, 90, 100 Hz for the magnitude data. It seems unlikely that there were actual sources of signal at all of the observed frequencies present in seawater. Most probably, the system captured reflections of 60 Hz signal and its higher harmonics due to cross-talk of electrode wires. This phenomenon was not observed in the initial lab testing because of the different wire arrangement. The signal cross-talk can be minimized in the future deployments by improving shielding for each of the electrode wires (similarly to the approach used for wiring compass module).

4.6. Effect of AC/DC stray currents on corrosion data from field trials

The data on the strength of AC and DC electric fields can be processed to estimate the effect of the observed stray currents on the collected corrosion data during the field trials at the same location. Following the approach of Jenkins (2001), the exchange electric current of corrosion reaction can be compared to the electric currents in the observed electric field.

The exchange current density is related to the corrosion rate by Faraday’s law (ASTM G102-89)

\[
\alpha = K_i \frac{i \cdot EW}{\rho}
\]  

(4.1)

where \( \alpha \) is the corrosion rate in \( \text{mm/year} \);

\( i \) is the current exchange density in \( \text{A/m}^2 \);

\( K_i = 327.2 \cdot \frac{\text{mm}}{\text{year} \cdot \text{A} \cdot \text{m}} \) is the constant from Table 2 in ASTM G102-89.

\( EW \) is the equivalent weight from Table 2 in ASTM G102-89.

\( \rho \) is the metal density in \( \text{kg/m}^3 \).
For example, for the seawater corrosion of copper plate (UNS C12200, \( \rho = 8,700 \) kg/m³, \( EW = 31.77 \)) with dimensions 180 x 50 x 3 mm³ at a rate of \( \alpha = 0.014 \) mm/year, the exchange current density is

\[
i = \frac{\alpha \cdot \rho}{K_e \cdot EW} = \frac{0.014 \cdot 8,700}{327.2 \cdot 31.77} = 11.7 \text{ mA/m}^2
\]

and the corresponding electric current is

\[
I = i \cdot A_s = 11.7 \text{ mA/m}^2 \cdot 0.202 \text{ m}^2 = 2.3 \text{ mA},
\]

where \( A_s \) is the surface area of the plate.

Thus, if this plate were subjected to the external anodic current of 0.24 mA, the corrosion rate would double. The voltage corresponding to 0.24 mA can be calculated by Ohm’s law

\[
E = I \cdot R
\]

where \( I \) is the electric current in A;

\[
R = \rho_w \cdot L \cdot A^{-1}
\]

is the resistance of seawater in Ω;

\[
\rho_w = 0.23 \Omega \cdot m
\]

is the seawater resistivity calculated from the specific conductance measurements;

\( L \) is the length of seawater column in m;

\( A \) is the cross-sectional area of the seawater column in m².

Rearranging (4.2) in terms of the electric field magnitude (by diving both sides by \( L \)) yields

\[
\Delta E = I \cdot \rho_w \cdot A^{-1}
\]

If we assume that the direction of stray current coincides with the normal to the surface of the plate, the electric field magnitude corresponding to the current of 0.24 mA is

\[
\Delta E = I \cdot \rho_w \cdot A^{-1} = 0.24 \text{ mA} \cdot 0.23 \Omega \cdot m \cdot (0.18 \cdot 0.05 \cdot m^2)^{-1} = 6.1 \text{ mV/m}
\]

Therefore, the corrosion rate of the copper plate doubles if there is 6.1 mV/m DC stray current in the presence of a structure cathodic to the plate. The maximum observed mean magnitude of DC electric field in the field testing was 2.0 mV/m and therefore it could affect
the corrosion rates by no more than 33%. The worst-case scenario would be if the direction of stray current were aligned with the path between the plate specimen and a remote cathode. Overall mean magnitude of DC electric field from the 30 days of deployment was 1.5 mV/m which corresponds to the 25% of potential increase in the corrosion rate.

Effect of the AC stray currents can be estimated in a similar way by comparing the maximum amplitude of AC electric field to the magnitude the field required to double the corrosion rate. The observed AC stray currents had amplitude of 1 mV/m. Even in the worst case of geometrical arrangement of copper plate and remote cathode, the increase in corrosion rate should not exceed 16%. However, this estimate is conservative because AC stray currents are known to have significantly lower effect on the corrosion rates compared to DC stray currents of the same magnitude (Wakelin et al., 1998). Therefore, for the given values, the effect of AC stray currents on the corrosion rates can be considered as negligible.

4.7. Future design suggestions

Based on the performance analysis of the developed system, the following design modifications are suggested for the future deployments:

(1) Noise floor of the system can be reduced by improving the shielding of the electrode wires. It can be achieved by following the same procedure as for wiring digital compass module.

(2) To improve accuracy of predictions of the effect of stray currents on the corrosion rates, current magnitude should also be recorded. This can be achieved by using additional inputs of the DAQ system.

(3) Since the system was capable to successfully operate with a very old CPU, the power consumption can be significantly reduced by switching to a single-board computer with a new low-voltage ARM or x86 processor.

(4) To reduce the cost, commercial DAQ system can be replaced with a custom-made DAQ with high-gain preamps.

(5) With steps (3) and (4) implemented, the control system can be packed into a single battery-operated package. This will allow to deploy the control system underwater.
Chapter 5. Mechanical Testing and Numerical Modeling of Copper Alloy Nets

In this chapter, mechanical testing is conducted to characterize copper alloy plates and structural components of chain-link nets. In particular, the effect of one-year seawater exposure on the mechanical properties of copper alloy plates is analyzed through the uniaxial tension tests. The testing data is processed to establish the changes in elastic properties, ultimate strength and ultimate strain, following the relevant ASTM standards. Stress-strain dependence is obtained for each of the tested materials using the digital image correlation technique. Some degradation of tensile strength is observed in all alloys, but for most of them, it is not substantial. Additional tests are performed on one of the alloys to characterize its elasto-plastic behavior in a wire and picket (element of a chain-link net panel) forms. This data is used to develop and validate a numerical model of the tensile response of a picket. The behavior of a chain-link net panel and double-loop netting connector is characterized through the tension tests to determine the structural response and failure modes of these components.

5.1. Mechanical testing of copper alloys plates

5.1.1. Experimental setup for uniaxial tension tests

Mechanical testing was carried out to characterize stiffness, strength, and ductility of the copper alloys investigated for seawater performance as discussed in Chapter 3. Standard tension tests (following ASTM E8/E8M) were performed on both virgin and weathered (i.e. subjected to a year of exposure to natural seawater) specimens to evaluate the effect of seawater exposure on their mechanical properties. The "dog-bone" samples were cut out of the original plates as shown in Fig. 5.1a. This cutting scheme allowed to produce three test specimens from each plate (denominated in the text to follow as E1 and E2 for edge specimens, and C for the specimens from the central part of the plates), and to reserve a strip for metallographic studies.

All experiments were performed on the servohydraulic testing machine INSTRON 1350 with a digital controller. Force measurements were recorded using an integrated 100 kN force transducer. The tests were performed at constant crosshead velocities of 0.08 mm/min for a total of 0.1 mm (up to about 0.5% strain) and after that at 1.66 mm/min up until the
failure. The selected strain rates are within the allowable crosshead velocity limits defined by ASTM E8/E8M-08. The data on deflections was recorded using two techniques: bonded resistance strain gages and digital image correlation.

Strain gages were used to determine the elastic properties (Young's modulus and Poisson's ratio) of the virgin specimens. The tee rosette strain gages were applied to both back and front surfaces of the specimen (Fig. 5.1b) to compensate for the bending effects due to load frame misalignment and/or slight longitudinal curvature of a specimen. They were attached to quarter Wheatstone bridges (Sharpe, 2008) assembled from 350 Ohm precision resistors. The strain gage and force transducer data was collected using 16-bit ADC board (Keithley KUSB-3108) at the data acquisition rate of 1 kHz, and averaged down to 10 Hz. The strain gage voltage measurements were converted to strain data using the formulae for quarter-bridge configuration corrected for bridge nonlinearity (Sharpe, 2008). Table 5.1 presents the measured Young's moduli and Poisson's ratios for all tested materials. This data represents the averages from five experiments on each material; the observed variations were within 3%. The average contribution of bending to the measured strains was found to be less than 5%. No significant difference was observed between the values for virgin and weathered specimens of the same alloy. Thus, we concluded that surface corrosion of the specimens does not affect the bulk material stiffness.

Fig. 5.1. (a) Corrosion specimen cut into subsize plates with reduced cross-section for mechanical testing. (b) Dogbone specimen with strain gages attached on opposite faces.
A commercial optical measurement system for 3D digital image correlation (3D DIC, Orteu, 2009; Sutton et al., 2007) was used to capture plastic strains and determine the ultimate tensile strains. The system consists of a set of two digital cameras, configured to acquire stereo images of the specimen surface, and post-processing software (www.correlatedsolutions.com). The testing setup is shown in Fig. 5.2. In contrast to contact strain measurement methods, such as extensometers, this technique does not induce premature necking and has an advantage of capturing a full strain field. Also, when compared to strain gages, this approach allows for measurements of a larger range of strains.

Table 5.1. Measured values of elastic parameters averaged from five experiments on each material.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Young's modulus, GPa</th>
<th>Poisson's ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>102</td>
<td>0.35</td>
</tr>
<tr>
<td>Br-2</td>
<td>109</td>
<td>0.31</td>
</tr>
<tr>
<td>Br-3</td>
<td>109</td>
<td>0.32</td>
</tr>
<tr>
<td>Br-4</td>
<td>110</td>
<td>0.32</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>124</td>
<td>0.30</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>139</td>
<td>0.29</td>
</tr>
<tr>
<td>CuSi</td>
<td>113</td>
<td>0.36</td>
</tr>
<tr>
<td>CuTin</td>
<td>120</td>
<td>0.34</td>
</tr>
<tr>
<td>Cu</td>
<td>132</td>
<td>0.27</td>
</tr>
<tr>
<td>Steel</td>
<td>208</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Fig. 5.2. 3D DIC testing setup.
The specimen preparation for 3D-DIC includes cleaning of the surface of interest, priming it with a white matte background, and application of random black speckles using a spray paint. The speckle size (around 2-3 px for the smallest speckles) is chosen based on the guidelines provided by the software developer (Correlated Solutions, 2010).

5.1.2. 3D-DIC data processing procedure

Prior to each testing session, the available 3D DIC system required calibration to establish intrinsic (lens and sensor distortions) and extrinsic parameters (relative position and orientation of the cameras) of the system components (see discussion in Sutton et al., 2007). The calibration was performed following the procedure recommended by the software developer (Correlated Solutions, 2010). All tests were conducted using a similar setup with 35-mm lenses, stereo-angle of around 10° and camera baseline distance of about 70 mm. With this setup, the calibration procedure resulted in average epipolar projection errors (definition of an epipolar error can be found in Orteu, 2009) of about 0.02 px.

The choice of post-processing parameters (subset size and stepping) for 3D DIC images can significantly affect the quality of the extracted strain data (see discussion in Pan et al., 2008). One of the parameters, subset size, defines the dimensions in pixels of a square window for tracking the deformations of speckle pattern on the specimen. This parameter directly affects both spatial resolution and strain sensitivity: with larger subset size the strain sensitivity is improved, however the spatial resolution is reduced. The other parameter, stepping, defines the step in pixels between the two adjacent subset windows. The stepping corresponds to the number of extracted data points per image.

The subset size of 29 px and stepping of 2 px were established after performing sensitivity studies using the collected data for pure copper virgin specimens. It was found that the subset size lower than 21 px resulted in large noise in the extracted strain measurements, and that at subset sizes larger than 33 px, the spatial resolution was too low for the used specimen geometry/magnification factor (the width of the specimen’s reduced section is about 6 mm or 120 px). The subset size of 29 px corresponds to the average point-to-point strain measurement error of 60 με. The stepping of 2 px corresponds to approximately 10,000 data points in the reduced section of the specimen. Fig. 5.3 illustrates the dependence
of displacement, strain, in-plane coordinate (x), and out-of-plane coordinate (z) errors on the subset size. Fig. 5.4 shows an example of the 3D-DIC data.

The strain data was extracted using two methods: full-field average from the reduced section area and a virtual extensometer attached to the ends of the reduced section area. In both cases, engineering strain formulation was used. It was found that the measurements from both techniques coincide in the uniform elongation range (prior to strain localization due to necking). However, slight difference was observed in the measurements with the onset of necking. It was decided to use the virtual extensometer measurements to be consistent with the traditionally used methods.

The same set of virgin specimens that was used for elastic properties determination using strain gages (denominated VC because it was cutout from the central piece), was also used to compare the 3D-DIC and strain gage measurements. Strain gages on one of the specimen faces were peeled off to apply the speckle pattern; and the specimens were tested

Fig. 5.3. Dependence of average (a) displacement errors, (b) strain errors, (c) x-coordinate errors, (d) z-coordinate errors on the subset size.
Fig. 5.4. Example of the extracted 3D-DIC data for pure copper virgin specimen (V-C): (a) distribution of \( \varepsilon_{yy} \)-strains overlaid on the captured image; (b) \( \varepsilon_{yy} \)-strain distribution plotted on the reconstructed 3D surface of the specimen.

up until failure. Fig. 5.5 illustrates the example of the collected data for Br-1 specimen. It can be seen that the strain gage and 3D-DIC data show good correlation (approximately 1% average deviations) in the full tested range (0.2% - 6% when the strain gages peeled off) for longitudinal and transverse strain measurements.

5.1.3. Measured changes in strength and ductility due to seawater exposure

Figures 5.6 and 5.7 illustrate the stress-strain data collected for all tested materials from central specimens before (denominated VC) and after (denominated XC) one-year exposure to seawater in the untensioned configuration. Table 5.2 summarizes the observed changes in the tensile strength of the considered materials. Note that the tensile strength values presented in column 3 of Table 5.2 were calculated using the initial (unexposed) thickness of the plates. We believe that such strength values calculated with respect to nominal cross-section area are more meaningful for engineering design and analysis purposes. In addition, the last column provides the values recalculated using the reduced area based on the
Fig. 5.5. Example of the combined measurements with strain gages and 3D DIC: stress-strain data for (a) longitudinal and (b) transverse strains. (c) strain gage vs. 3D-DIC data plot for elastic strain range.
Fig. 5.6. Stress-strain data obtained using 3D DIC for specimens 1-6 from the virgin material (VC) and exposed material central specimens (XC).
Fig. 5.7. Stress-strain data obtained using 3D DIC for specimens 7-B from the virgin material (VC) and exposed material central specimens (XC).
Table 5.2. Changes in ultimate tensile strength [UTS] and strain [UES] of copper alloys due to one-year seawater exposure.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>UTS for virgin [MPa]</th>
<th>UTS after 1 year [MPa]</th>
<th>Change in UTS [%]</th>
<th>UTS with adjusted thickness [MPa]</th>
<th>UES for virgin [%]</th>
<th>UES after 1 year [%]</th>
<th>Change in UES [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br-1</td>
<td>303</td>
<td>299</td>
<td>-1.5</td>
<td>301</td>
<td>81.5</td>
<td>84.2</td>
<td>2.7</td>
</tr>
<tr>
<td>Br-2</td>
<td>358</td>
<td>354</td>
<td>-1.0</td>
<td>356</td>
<td>65.4</td>
<td>66.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Br-3</td>
<td>396</td>
<td>366</td>
<td>-7.5</td>
<td>368</td>
<td>57.0</td>
<td>62.5</td>
<td>5.5</td>
</tr>
<tr>
<td>Br-4</td>
<td>572</td>
<td>568</td>
<td>-0.6</td>
<td>569</td>
<td>40.4</td>
<td>40.6</td>
<td>0.2</td>
</tr>
<tr>
<td>CuNi-1</td>
<td>340</td>
<td>334</td>
<td>-1.8</td>
<td>335</td>
<td>33.4</td>
<td>33.3</td>
<td>-0.1</td>
</tr>
<tr>
<td>CuNi-2</td>
<td>537</td>
<td>522</td>
<td>-2.8</td>
<td>527</td>
<td>37.0</td>
<td>37.9</td>
<td>0.9</td>
</tr>
<tr>
<td>CuSi</td>
<td>472</td>
<td>465</td>
<td>-1.7</td>
<td>467</td>
<td>55.1</td>
<td>53.9</td>
<td>-1.2</td>
</tr>
<tr>
<td>CuTin</td>
<td>498</td>
<td>496</td>
<td>-0.4</td>
<td>497</td>
<td>34.9</td>
<td>34.4</td>
<td>-0.5</td>
</tr>
<tr>
<td>Cu</td>
<td>401</td>
<td>401</td>
<td>0.0</td>
<td>403</td>
<td>8.0</td>
<td>8.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Steel</td>
<td>394</td>
<td>395</td>
<td>0.1</td>
<td>417</td>
<td>34.9</td>
<td>40.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

corrosion rates presented in Table 3.7. As can be seen from the table, degradation of the nominal tensile strength is under 2% for most of the materials with slightly more pronounced drop in strength for Br-3 and CuNi-2 (7.5% and 2.8%, correspondingly). Correlation of the behavior of these alloys to their composition and microstructure (e.g. grain size) requires further investigations. Some insignificant increase in strength was observed for the steel specimen. It is attributed to the variations of material properties within the batch. The last three columns of Table 5.2 present exposure-induced changes in the ultimate strain of the tested materials. It appears that exposure to seawater increases the ultimate strain in Zn-containing copper alloys and pure copper.

5.2. Mechanical behavior of pickets in copper alloy chain-link nets

Chain-link nets are composed of interconnected individual bent wires or "pickets" (see Fig. 5.8). The pickets are manufactured from the straight wires by bending them in a chain-link weaving machine. It is expected that the mechanical response of pickets defines the structural properties of a chain-link net. Therefore, to make reliable predictions of strength and service life of these nets, it is important to understand and characterize the mechanical behavior of the pickets.
5.2.1. Experimental testing of copper alloy wires

Due to the differences in manufacturing process, the stress-strain behavior of plate specimens (presented in Figures 5.6 and 5.7) may differ from that of wire specimens (differences in heat treatment and effects of cold working). Standard tension tests following ASTM E8/E8M were performed on Br-1 wire specimens with diameter of 2.5 mm and length of 120 mm. The specimens were fixed using the wedge grips (also used for picket testing, see Fig. 5.10) instead of the grips recommended in ASTM E8/E8M due to the issues with specimen necking at the attachment points. The tests were conducted at constant crosshead velocity of 10 mm/min up to the failure. Force measurements were recorded using an integrated 100 kN force transducer, and the deflections were recorded using an integrated LVDT crosshead displacement sensor.

The obtained stress-strain curves for the wire specimens are presented in Fig. 5.9. As previously suggested, the stress-strain response of the wires shows significantly different behavior: the strength is increased about 2x and ductility is reduced approximately 4x. Significant scatter in ultimate strain (19.4%-22.5%) of wire specimens is also observed, which may suggest that at this scale (diameter of 2.5 mm) relatively large grain sizes induce plastic instabilities and control the onset of necking.

Fig. 5.8. Structural elements of a chain-link net panel: (a) wire, (b) picket, (c) the net itself - series of interconnected pickets forming the mesh.
5.2.2. Experimental testing of copper alloy pickets

Tension tests were performed on picket sections to evaluate the apparent tensile strength and stiffness of the pickets. The specimens were fixed in the wedge grips (see Fig. 5.10) using the same setup as for the plate and wire testing (see Sections 5.1.1 and 5.2.1). The specimens were manufactured from the same spool of wire as the tested wire sections. The picket geometry has width $W = 23 \, \text{mm}$ and pitch $P = 46 \, \text{mm}$ (see Fig. 5.8b), and the length of tested section is approximately 2.5 spiral revolutions. Fig. 5.10 illustrates the evolution of picket shape throughout the testing and up to the failure. It is interesting to note that due to the sufficient ductility of the wire material, the picket is capable to fully unfold back into the wire shape, and then fails after necking similar to the failure mode of the wire.

Fig. 5.11 illustrates the obtained force-displacement data for the three tested pickets. It can be observed that the mechanical response to the tension load can be characterized by the four regions with distinct differences in apparent stiffness: (1) linear response up ca. 100 $N$; (2) highly nonlinear response with a significant increase in stiffness up to ca. 900 $N$; (3) quasi-linear response with slightly increasing stiffness up to ca. 2,200 $N$; (4) nonlinear response with decreasing stiffness up to failure at ca. 2,600 $N$. These distinct changes in the
apparent stiffness can be explained by the observed evolution of the picket shape (Fig. 5.10). In the region (1), the picket undergoes small deformations (mostly elastic) with minimal plastic effects concentrated in the spiral bends. Region (2) corresponds to the significant changes in the picket shape leading to the gradual straightening (and therefore increasing

![Image of picket deformation history](image-url)

**Fig. 5.10.** Deformation history of a picket: from initial to the final shape right before failure.

![Graph of force-displacement data](image-url)

**Fig. 5.11.** Force-displacement data for the tested pickets made of Br-1.
stiffness). In this load range, significant plastic deformations occur at the bends and in the surrounding areas with little deformation in the straight sections of the picket. In the region (3) the picket shape corresponds to that of an almost straight wire with gradual evolution into a fully straight wire. Therefore, due to small changes in specimen shape, the response is quasi-linear with slight increase in the stiffness. In the final stage (corresponding to region 4), the plastic deformations spread along the total length of the specimen leading to the gradual decrease of the stiffness, onset of necking, and eventual failure.

5.2.3. FEA simulations of mechanical behavior of a picket

A finite element model was developed to simulate the mechanical response of a picket under the same loading conditions as in the tensile test described in Section 5.2.2. The geometry was constructed in a commercial CAD software (SolidWorks 2010) based on the dimensions of an actual picket (see Fig. 5.12). The finite element mesh, consisting of 30,000 second-order isoparametric tetrahedrons, was generated using the meshing feature of the software. The meshing parameters were set as follows: average element size of 1 mm,
minimum of 12 elements per circle, and growth factor of 1.25. An additional refined mesh was generated (80,000 elements, average element size of 0.5 \textit{mm}, 16 elements per circle) to investigate the sensitivity of simulation data to the level of discretization.

The finite element mesh was exported to the MSC Marc commercial finite element solver. The boundary conditions from the actual test (gripping with the wedge grips and crosshead displacement of the bottom grip) were simulated by fixing nodes of the top face of the picket, and prescribing linearly increasing displacement to all nodes of the bottom face. The material properties were assigned as elasto-plastic isotropic constitutive model with von Mises yield criterion and isotropic hardening. The elastic constants were used from Table 5.1 and plastic behavior was assigned as a table with experimental data for the wires made of the same material (see Fig. 5.9). Before importing the plasticity data into the software, the engineering stress-strain data was converted to the true stress-equivalent plastic strain format, smoothed and extrapolated as shown in Fig. 5.13. The residual stresses due to forming of a picket were not considered (zero pre-stresses). The solver parameters were set as follows: large strain/displacement formulation; automatic load stepping (not larger than 0.2 \textit{mm} per increment); direct matrix solver; residuals and displacement convergence criteria with tolerance of 0.001.
Fig. 5.14 shows the predicted evolution of plastic strains throughout the test, and Fig. 5.15 provides comparison of the simulated load-deflection response with the experimental data (test 3 from Fig. 5.11). Good correspondence of the predicted and the actual elasto-plastic response is observed. It is suggested that residual stresses in the picket (due to forming from a straight wire) can be neglected in the simulations of the mechanical response of pickets.

**Fig. 5.14.** Evolution of equivalent plastic strains throughout the virtual tension test at crosshead displacements (left to right): 10, 30, 50, 70, 94 mm.

**Fig. 5.15.** Comparison of the force-displacement data obtained from the finite element simulation and mechanical tests for chain-link picket made of Br-1.
5.3. Mechanical behavior of chain-link nets

Even though the mechanical behavior of individual pickets provides a good estimate of the response of chain-link nets to the tensile loads in the direction of pickets, this information is insufficient to accurately predict the response in the transverse direction (perpendicular to the picket direction). Modeling of transverse mechanical behavior requires complex highly nonlinear simulations, which take into account picket-to-picket contact. Therefore, it is important to perform the experimental testing to characterize the apparent stiffness and strength in that direction.

One of the issues with tension testing of chain-link net panels is that it is not standardized, and the literature search on this topic did not reveal a universally adopted type of fixtures for this testing. The author designed a custom set of fixtures for tension testing of chain-link net panels as illustrated in Fig. 5.16. This design was chosen due to its simplicity and high rigidity, along with the ease of securing/removing of a net panel. The net panels are attached using the "double-loop" connectors (see Section 5.3.2 for details) which are widely used in the industry for connecting and attaching the net panel sections.

Fig. 5.16. Custom-designed fixtures for tension testing of chain-link net panels.
5.3.1. Experimental testing of transverse tensile strength of chain-link net panel

Transverse tension tests were performed on a chain-link net panel using the same testing machine as for the testing of pickets and wires. The specimens were fixed in the custom-made grips with double-loop connectors. Due to the limited stroke of the testing machine (100 mm), only a narrow section consisting of six pickets could be tested. Note that to simulate the worst-case loading scenario, the net panel was secured to the testing frame in such a way that the contraction of the panel was not allowed. This was achieved by placing the outmost connectors beyond the outmost shackles. Fig. 5.17 provides the force-displacement data for the entire test up to the failure of all pickets.

Fig. 5.18 illustrates evolution of the net panel shape throughout the testing up to the failure. Fig. 5.18c shows the net panel shape right after the failure of the first picket. The obtained data distinctly shows the points of failure for each of the pickets. It is interesting to note that the overall response of the net panel up to failure of the first picket can be approximated as a linear fit connecting the origin (0,0) and the point at failure. Based on the visual analysis of the recorded test images, the observed deviation from linear response (dip in the range ca. 7-20 kN) can be explained by the slight geometry rearrangement between the pickets and a significant “bowing” of the net panel in this load range.

![Force-displacement data for the transverse tension test of a chain-link net panel.](image)

Fig. 5.17. Force-displacement data for the transverse tension test of a chain-link net panel.
Fig. 5.18. Deformation history of a chain-link net panel under transverse tension: (a) initial shape, (b) deformation right before failure; (c) final shape at failure.
5.3.2. Experimental testing of tensile strength of chain-link net connectors

Additional tension tests were performed to evaluate the apparent strength of double-loop connectors which are widely used in the industry for securing and connecting the net panels. The connectors were tested using the same testing machine as for the testing of chain-link net panels. The specimens were secured between two clevis grips with bearing-loading rods (see Fig. 5.19). The double-loop connectors were manufactured in-place from the double-wire sections by twisting them symmetrically (to at least three turns) at the intersection. Fig. 5.20 provides the force-displacement data from one the tests. Comparing

Fig. 5.19. Deformation history of a double-loop netting connector: from initial to the final shape at failure.

Fig. 5.20. Force-displacement data for the tested double loop netting connector.
the visual data to the mechanical response curve, it can be observed that these components fail progressively due to the untwisting of the loop and slipping of the opposite ends of the wire. This behavior (untwisting of the loop instead of strain localization in the wire) was not expected. It is attributed to the high ductility of the copper alloy (Br-1). This mode of failure is strongly dependent on the friction between the wires and the quality of the initial twisting (which was observed in the preliminary testing).

5.4. Major observations from mechanical testing of copper alloy chain-link net components

Analysis of the mechanical behavior of copper alloy plates before and after one-year exposure to natural seawater shows no significant changes in the elastic stiffness. The changes in ultimate strength are not very significant either, indicating very limited localized corrosion damage (as follows from the column 5 of Table 5.2). We conclude that the nominal tensile strength is reduced mostly due to the corrosion-driven material loss. Furthermore, the stress-strain data (adjusted for the reduction in thickness) of the virgin specimens provides a good estimate of the mechanical behavior after one-year of seawater exposure.

Mechanical testing of a chain-link picket under tensile load shows that its longitudinal deformation occurs in four major steps: (1) linearly elastic deformations with insignificant plastic deformations in the spiral bends; (2) increasing plastic deformations (shearing) of the spiral bends leading to the straightening of the picket; (3) elongation of the straight sections of the pickets with minor shape changes (quasi-linear apparent stiffness); (4) spreading of the plastic deformation throughout the straightened picket with subsequent necking and failure. This behavior is accurately reproduced by a 3D finite element model based on the experimentally obtained elasto-plastic properties of the material.

It is observed that the force-displacement behavior of a chain-link net panel under transverse tensile loading can be approximated as quasi-linear up to the initiation of pickets' failure. Testing of the double-loop connectors shows that these components fail by untwisting of the wires instead of necking. Such a behavior is attributed to high ductility of the material (Br-1).
Chapter 6. Design and Modeling of Submersible Fish Cages with Copper Netting for Open Ocean Aquaculture

This chapter deals with introduction of copper alloy nets in open ocean aquaculture as a new technology to reduce biofouling, improve cage volume stability, its structural strength, and to provide additional protection from predators. Novel design and fabrication procedures are discussed for engineering of the offshore fish farms utilizing copper alloy netting. These procedures are illustrated on a commercial size gravity-type offshore fish cage, which was designed and successfully deployed in the Pacific Ocean near Isla Italia (Patagonia, Chile).

6.1. Engineering challenges for utilization of copper alloy netting in marine aquaculture

In a typical marine aquacultural operation, fish are raised in cages consisting of a buoyant framework with a suspended net chamber (gravity-type cage). Weights are added to the net to help retain its shape and volume. Some cages have rigid superstructure to which the net is attached, eliminating net deformation (for example, SeaStation™, AquaPod™ net pens, see Fredriksson et al., 2004; Loverich and Gace, 1997).

The fish cages can be either surface-type (floating on the surface) or submersible to mitigate the effects of high-energy surface conditions and improve the fish growing environment. Traditionally, net chambers are made of nylon netting in both inshore and offshore fish farms. Potential improvements in fish farming operations and maintenance can be achieved by substituting polymer nets with copper alloy netting. Usage of the latter in offshore aquaculture requires new design techniques and revised analysis procedures due to a different set of physical properties (density, stiffness, strength) as compared to nylon and polyester which are traditionally used for fish cage netting.

This chapter deals with introduction of copper alloy nets in open ocean aquaculture as a new technology to reduce biofouling, improve cage volumetric stability and its structural strength, and provide additional protection from predators. Development of fouling- and predator-resistant copper alloy netting technology started in 1970s with enclosures for
salmon farming in the Northeast USA. Initial trials documented that after six years of deployment, enclosures had very little biofouling and minimal losses due to predator attacks (Efird, 1975; Efird and Anderson, 1975; Huguenin and Ansuini, 1975). It is estimated that more than 300 cages utilizing copper alloy nets are currently installed in Australia, Chile and Japan. The use of copper alloy net materials has shown promising results in gravity-type and rigid-frame cages located in protected areas, such as bays and fjords (Ansuini and Huguenin, 1978; Huguenin et al., 1981; DeCew et al., 2010a). Biological growth on copper alloy net chambers is minimal compared to the nylon net pens, allowing improved fish growth rates and oxygen flow, decreased maintenance and cleaning costs. Note that in the text to follow we refer to various copper alloy nets simply as “copper nets”.

However, there are several difficulties associated with wide adoption of this new technology by the marine aquaculture industry. They include:

- Increased initial costs due to high material costs of copper alloys and necessity to improve structural strength of the cage framework;
- Need for modification of design and installation techniques to integrate copper nets into the existing industry;
- Difficulties in handling components during cage fabrication and deployment due to the substantially increased weight of the system both dry and in water.

Design of marine aquaculture fish farms follows well established procedures, as reflected, for example, in the Norwegian Standard NS 9415.E. These procedures were developed for systems with polymer nets, deployed primarily on the sea surface (non-submersible) in low energy environments characterized by significant wave heights lower than 3 m and currents lower than 1.5 m/s. In this chapter, we propose modifications required for successful utilization of copper nets in fish farms deployed in both protected and exposed locations.

Fish cages with copper netting should be designed in such a way that existing aquacultural technologies and practices are used with few changes to accommodate the new netting type. This approach allows for easy integration of these systems into the existing industry (i.e. through retrofitting of the existing fish cage systems) and provides a
lower economical barrier to the introduction of this technology. Advantages of copper netting can be summarized as follows:

- enhanced water flow through the cage, reduced parasites and infections due to significantly lower biofouling;
- reduced mortality of fish due to better protection from predators;
- lower maintenance and operational costs: no net changes; no net cleaning, no need for predator nets and lower use of antibiotics;
- reduced environmental impact: copper alloys can be recycled after fish cage recovery, no need to dispose of bio-fouling as with polymer nets.

In this chapter, the procedures to design and fabricate a marine aquaculture system with copper alloy netting are presented on the example of a fishcage in a single-bay mooring grid designed in collaboration with EcoSea Farming S.A. (Chile) and deployed in the South Pacific. Two identical cages were successfully deployed in inshore and offshore sites, proving the flexibility of the design. More detailed information can be found in the project report (Celikkol et al., 2010).

6.2. Design approach and constraints

Fish cages can be divided into three major categories with respect to their structural design using an approach similar to the one proposed in (Loverich and Gace, 1997). Gravity type flexible cages rely on a combination of upper structure (floater) buoyancy and lower structure (ballast rim or system of sinkers) weight to maintain the shape and volume of fish containment chamber. In tension-leg systems, the forces from pre-tensioned mooring lines are used instead of weights to stabilize the fish cage volume. Rigid-frame cages retain their volume and shape due to the stiffness of frame. The examples of all three fish cage types are provided in Fig. 6.1. Note that all three of them can be used in both surface and submerged regimes with some design modifications and proper choice of a mooring configuration.
High initial costs of offshore aquacultural systems (especially, the ones with copper alloy components) demand systematic engineering approach during all stages of design and construction. The deployed system should withstand service loads as well as survive without substantial damage through the storms inadvertent in the high-energy deployment locations. At the design stages, it is important to ensure that the structural strength is adequate and that the fish cage dynamic behavior is steady enough for a successful farming. This can be achieved through the structural strength analysis and dynamic simulations for both service and storm conditions. Recent developments of the computational techniques (Bessonneau and Marichal, 1998; Tsukrov et al., 2003; Jensen et al., 2007; Lee et al., 2008) allow for a robust analysis of the investigated design prior to the physical testing and field deployment. Proper engineering procedure for the development of an offshore fish cage system with copper alloy components should include the following steps:

- Obtain environmental data for the planned fish farm location;
- Select appropriate fish cage type and mooring system configuration;
- Establish the design constraints, operational limits and service life requirements;
- Generate several candidate designs; for each design, analyze hydrostatic characteristics and perform sizing of major components;
- Select the best configuration and develop the first design iteration including detailed drawings of all system components;
• Analyze structural integrity and dynamic response of the individual components and system as a whole; analyze material compatibility (e.g. make sure steel components are securely isolated from any copper parts to prevent galvanic corrosion); design suitable copper net attachments, which ensure net pen integrity and limit wear of the netting;

• Perform design reviews with construction/operations personnel; address potential handling issues during assembly/construction/deployment; produce assembly/construction/deployment plans;

• If possible, perform scaled physical testing;

• Finalize the design and produce detailed documentation.

Note that some steps are interdependent and therefore should be performed simultaneously. Some of these steps are presented in the following sections in more detail to illustrate the aspects of engineering process dealing with copper nets.

The proposed design consists of a 20 m diameter gravity-type cage (see Fig. 6.2) with the netting suspended from the top rim and attached to the bottom rim, which is required to maintain volumetric stability. Framework consists of two surface pipes supported by the brackets on top and a single pipe of the same diameter on the bottom. The entire net chamber is fabricated from the copper alloy chain-link net. An airlift-ballast assembly is added to the system to allow the cage to quickly surface and submerge. A single-bay grid mooring (with redundant anchor legs for safety) is utilized to secure the fish cage system. A hydraulic venturi-style feed device is used to feed the fish when submerged for extended periods of time.

The design should satisfy the following requirements:

• Provide 3,000 m³ net pen for fish farming;
• Sustain net chamber integrity and volumetric stability in a variety of environmental conditions;
• Provide sufficient reserve buoyancy for on-cage surface operations and maintenance;
• Allow for quick submergence to avoid red tides / toxic algae outbreaks;
• Withstand loads in a high-energy environment.
6.3. Development of candidate designs

The design process started with a review of information on the environmental conditions at the proposed fish farm deployment location. Based on the available data, it was concluded that a load case representing storm events consisted of a 9-meter, 12-second wave with a collinear 1.5 m/s current. This loadcase was utilized for design and analysis purposes, along with a set of additional loadcases representing daily service conditions. It
was also established that surface operations should be limited, and it was recommended to submerge the system for fish grow-out. Thus, service life expectancy of the cage (specifically the net chamber) could be prolonged.

Next, preliminary cage and mooring configurations were developed for the selected environmental conditions. Overall cage design and mooring parameters such as diameter, volume, and construction materials were established. Dynamic analysis (numerical simulations) of a surface cage was performed to get a first-order estimate of net and mooring loads. Using the obtained information, possible net chamber connections were proposed, analyzed, and incorporated into the overall net pen. Preliminary finite element analysis was performed on all critical components to eliminate suspect cage configurations and component designs.

Several candidate designs were chosen for a more detailed study. Hydrostatic characteristics were determined for each of the prototype designs (Drach and DeCew, 2009). The vertical centers of mass and buoyancy of the fish cage were calculated and compared to verify stability. The reserve buoyancy of each system was calculated to insure proper working conditions.

With a preliminary cage and mooring design established, a series of design reviews were performed with participation of EcoSea engineers and Chilean aquaculture industry personnel. Suggestions to the cage configuration, net attachments, mooring design, surface and submerging operations were reviewed and implemented. The system was re-examined and adjusted as necessary to insure that structural integrity, manufacturing techniques and planned operational logistics were adequate and compliant with the industry standards in the region.

Several copper net configurations with different chain-link weaving orientations and net attachment methods were considered. Galvanic corrosion concerns, optimal net usage and proper fish containment during submerged operations were analyzed as well. System operating procedures and methods to assemble the cage and netting for candidate designs were developed. The mooring line lengths, diameters, and connections were specified, taking into account standard practices of the Chilean aquaculture industry. The layout and
major components are shown in Figures 6.3 and 6.4. Geometric, physical and material properties of each component were examined for compatibility. After the review, necessary modifications were incorporated and the candidate design configuration was finalized for detailed engineering analysis.

6.4. Numerical simulations of the overall dynamic response

The dynamic performance of the fishcage system was numerically modeled using the finite element analysis program AQUA-FE. This software package allows to perform the dynamic analysis of 3-D flexible structures in the marine environment. It was developed and maintained by the University of New Hampshire (Gosz et al., 1996; Tsukrov et al., 2000, 2003; Kestler, 2004) and has been successfully used with multiple ocean engineering projects (Fredriksson et al., 2003; DeCew et al., 2005, 2010b). Note that this kind of analysis can also be performed using other software packages (Le Bris and Marichal, 1998; Lader et al., 2003; Takagi et al., 2004; Zhao et al., 2007). The system was first analyzed with no wave or current forcing. This static simulation insured the model was constructed properly, and

Fig. 6.3. General mooring layout.
allowed to analyze the net chamber shape in as deployed configuration. The obtained hydrostatic parameters of the system in both surface and submerged configurations are summarized in Table 6.1.

After the model was verified in the hydrostatic analysis, numerical simulations were performed for two sets of environmental conditions in submerged (depth of 10 m) and surface configurations:

- Service loads: 5 m waves with period of 10 s and collinear currents 0.75 m/s
- Storm loads: 9 m waves with period of 12 s and collinear currents 1.5 m/s

For both loadcases, the waves and currents approached the system as shown in Fig. 6.5. The output data from the simulations was used to verify net pen stability and to size the mooring gear and anchor blocks. The following information was monitored during the numerical simulations: tensions at the anchors and anchor lines (see Fig. 6.6), grid/ballast/
Table 6.1. Distribution of buoyancy and weight within the fish cage.

<table>
<thead>
<tr>
<th>Assembly</th>
<th>Item</th>
<th>Weight, N</th>
<th>Buoyancy, N</th>
<th>Effective, N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Rim</td>
<td>Inner and outer pipes (filled with air)</td>
<td>62,230</td>
<td>168,740</td>
<td>106,510</td>
</tr>
<tr>
<td></td>
<td>Inner and outer pipe foam</td>
<td>2,000</td>
<td>0</td>
<td>-2,000</td>
</tr>
<tr>
<td></td>
<td>Bracket chains (13mm)</td>
<td>2,300</td>
<td>280</td>
<td>-2,020</td>
</tr>
<tr>
<td></td>
<td>Top brackets 1 and 2 (x18)</td>
<td>30,740</td>
<td>6,450</td>
<td>-24,290</td>
</tr>
<tr>
<td></td>
<td>Net pipe (filled with air)</td>
<td>3,670</td>
<td>9,910</td>
<td>6,240</td>
</tr>
<tr>
<td></td>
<td>Net pipe chain (16mm)</td>
<td>3,810</td>
<td>0</td>
<td>-3,810</td>
</tr>
<tr>
<td></td>
<td>Handrail pipe (flooded with water)</td>
<td>1,230</td>
<td>1,230</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Additional equipment</td>
<td>1,000</td>
<td>0</td>
<td>-1,000</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>106,980</strong></td>
<td><strong>186,610</strong></td>
<td><strong>79,630</strong></td>
</tr>
<tr>
<td>Side Netting</td>
<td>Netting</td>
<td>36,440</td>
<td>4,290</td>
<td>-32,150</td>
</tr>
<tr>
<td></td>
<td>Wire Support (200)</td>
<td>2,200</td>
<td>260</td>
<td>-1,940</td>
</tr>
<tr>
<td></td>
<td>Wire Double Loops (400) &amp; Outline</td>
<td>650</td>
<td>80</td>
<td>-570</td>
</tr>
<tr>
<td>Bottom Rim</td>
<td>Pipe (60% flooded with water)</td>
<td>29,850</td>
<td>32,080+19,520</td>
<td>21,750</td>
</tr>
<tr>
<td></td>
<td>Pipe Foam</td>
<td>380</td>
<td>0</td>
<td>-380</td>
</tr>
<tr>
<td></td>
<td>Bottom Bracket (x36)</td>
<td>17,400</td>
<td>4,130</td>
<td>-13,270</td>
</tr>
<tr>
<td></td>
<td>Net Pipe (filled with air)</td>
<td>3,670</td>
<td>9,910</td>
<td>6,240</td>
</tr>
<tr>
<td></td>
<td>Netting</td>
<td>18,220</td>
<td>2,150</td>
<td>-16,070</td>
</tr>
<tr>
<td></td>
<td><strong>SUBTOTAL</strong></td>
<td><strong>69,520</strong></td>
<td><strong>87,790</strong></td>
<td><strong>-1,730</strong></td>
</tr>
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<td></td>
<td><strong>CAGE TOTAL</strong></td>
<td><strong>215,790</strong></td>
<td><strong>259,030</strong></td>
<td><strong>43,240</strong></td>
</tr>
<tr>
<td>Airlift-ballast</td>
<td></td>
<td>55,000</td>
<td>-66,100</td>
<td>-11,100</td>
</tr>
<tr>
<td>On the surface (lift bag inflated)</td>
<td></td>
<td></td>
<td></td>
<td>32,140</td>
</tr>
<tr>
<td>Submerged (lift bag deflated)</td>
<td></td>
<td></td>
<td></td>
<td>-22,860</td>
</tr>
</tbody>
</table>

Fig. 6.5. Top view of the mooring system with the direction of applied waves and currents.
Fig. 6.6. The mooring anchor tensions for surface (top) and submerged (bottom) configurations.

Fig. 6.7. The grid line tensions in surface (left) and submerged (right) configurations.

Fig. 6.8. The surface (left) and submerged (right) prototype cage system surge and heave response from the storm load case.
bridle line tensions (see Fig. 6.7), motions of cage and floats (see Fig. 6.8). The heave response of floats was investigated to insure that the surface floats would not submerge greater than 5 m during this event (to avoid possible collapsing of float and loss of buoyancy within the mooring).

6.5. Fish cage design elements

The results of the dynamic analysis were used as input to a structural model of the system and its components. Structural modeling was performed using a commercially available CAE software package (SolidWorks). Finite element simulations of all load bearing components were conducted to investigate the structural integrity and establish the service load limits. Stresses at critical connections (e.g. mooring line and ballast bridles attachment points) were analyzed to optimize the material usage. A safety factor of 3.5, defined as a ratio of von Mises stress to the yield strength of the material, was set as the strength criterion. Note that the data from finite element analysis can sometime predict excessively high localized stresses (usually at sharp corners in the component geometry). Therefore, the design criterion is applied not to a single highest finite element stress observed in the analysis, but rather to the volume ratio of the elements. For example, no more than 0.1% of all elements by volume are allowed to fail the strength criterion.

6.5.1. Framework

A schematic of the cage system is presented in Fig. 6.2. The top superstructure (Fig. 6.9) consists of two pipes made of high density polyethylene (HDPE), a handrail, net support pipe (referred to as the “net pipe” in the text to follow) and 36 brackets. Both buoyancy pipes are 400 mm diameter DR9 pipes, providing the majority of the buoyancy and structural integrity of the system. These pipes are aligned with 18 brackets, as shown in Fig. 6.10a, which support the handrail (110 mm) and net pipe (140 mm). Mooring attachments are located on the outside of each bracket. The other 18 brackets (Fig. 6.10b), placed only over the inner buoyancy pipe, provide additional support to the net pipe. This allows for a more even distribution of the net chamber weight (ca. 5,400 kg) and dynamic loads on the structural pipe when subjected to waves.
A lower rim is incorporated into the design to help stabilize the volume of the net chamber, as well as provide some additional buoyancy to offset the net chamber weight. The rim is fabricated of HDPE pipes similar to the top superstructure, but without one buoyancy pipe and a handrail. Whereas the top rim has two sets of brackets, the lower rim assembly uses only one bracket modification (Fig. 6.10c) with a pad-eye for attachment of the ballast bridles.

Fig. 6.9. Top superstructure consists of a handrail, two main structural pipes and a net support pipe. The net chamber is attached to the net pipe on the top and bottom rims. The lower rim has only one structural pipe.

Fig. 6.10. Brackets designed for the system: (a) main top rim bracket that secures all top rims. (b) top rim support bracket with additional support for the net pipe; (c) bottom rim bracket with a net support component and a pad-eye for the ballast bridle system.
The framework pipes were evaluated to endure three different types of potential failure modes: (1) failure due to bending during the assembly; (2) failure due to hydrostatic pressure at the maximum depth of the deployment location; (3) buckling under the wave loads. Based on the manufacturer's guidelines, it was found that the selected combination of pipe diameter/thickness/cage diameter provide a safety factor of 1.23 for the first type of loading. For the second type of loading, it was found that for the selected configuration, the safety factor is 4.4. To investigate the behavior of the pipes under the third type of load, the numerical simulations were performed.

The buckling behavior of a structural pipe was analyzed for the worst-case scenario: single pipe taking the entire load during the storm event. The analysis was carried out using a commercial finite element solver (MSC Marc/Mentat) to determine critical load for elastic loss of stability and plastic buckling modes.

Single pipe of the top superstructure (or equivalently bottom rim) is made of HDPE with the diameter of 400 mm and wall thickness of 44.7 mm, and is bent and fused into a circle with the diameter of 20 m. The pipe is subjected to a uniformly distributed vertical load applied to the top half surface over the full length. Due to the rotational symmetry of the pipe shape (circle with 20 m diameter), only a quarter was analyzed with plane symmetry boundary conditions.

Pipe was meshed using constant thickness shell elements with the following parameters: first-order quadrilateral elements as element type; 5° discretization angle along the circumference (72 segments describing the pipe cross-sectional shape); 0.25° discretization angle along the length (1,440 cross-sectional segments). These parameters correspond to the total of 26,000 elements with an average element size of about 17 x 44 mm.

The material properties (HDPE) were assigned using the isotropic linear elastic-perfectly plastic constitutive model with Young's modulus of 0.667 GPa, Poisson's ratio of 0.42, yield strength of 24 MPa, and von Mises yielding criterion. The materials parameters were taken from the experimental data in DeCew (2011). This material model is very conservative because it assumes zero strength immediately after the onset of yielding.
Fig. 6.11. Boundary conditions for the cases with (a) eight and (b) sixteen supports. Finite element mesh is shown in detail in (c). Pink arrows represent symmetry constraints, yellow arrows represent constrained displacements in the vertical direction, green arrows represent the applied force.

Two loadcases were considered, representing the case when a total of eight and sixteen brackets are used around the circumference of the fish cage. The presence of brackets was simulated by constraining the nodes of the bottom half-surface of the pipe at the locations where actual brackets would be installed (see Fig. 6.11).

Simulations were carried out as nonlinear quasi-static loadcases with linearly increasing load. A software option to extract the first four buckling modes (eigenvalue stability solutions) at all load increments was selected to determine the critical loads for elastic loss of stability. This approach allowed to monitor critical elastic instability buckling load prior to the structure collapsing in the plastic buckling mode. This way it was possible to determine the lowest critical load for both buckling modes simultaneously.
Fig. 6.12. Distribution of von Mises stresses at the last increment before plastic buckling collapse for (a) 8-bracket and (b) 16-bracket loadcases. Both deformed and undeformed geometries are shown. Deformation scale is (a) 1:1 and (b) 3:1.

Fig. 6.12 provides the stress distributions obtained from the analysis. The simulation data shows that in both loadcases the elastic buckling critical loads are consistently higher than the critical plastic buckling load up until the plastic collapse. The plastic deformations start propagating in individual elements at the loads of 227.1 kN and 534.3 kN for 8- and 16-bracket loadcases, respectively. The pipe collapse due to plastic buckling occurs when the load reaches 382 kN (2.5% of elements plastically deformed) and 1,296 kN (2.8% elements plastically deformed), correspondingly. Thus, buckling will occur at the load of 382 kN which is equivalent to 1,528 kN for the full pipe (full 20 m diameter circle).

6.5.2. Airlift connection plate

Finite element analysis was used to model the mechanical response to dynamic loads of the airlift connection plate using the quasi-static loadcases. The geometry was designed in the CAD software (SolidWorks), and the analysis was performed using the Simulation
module of the software. The mesh (see Fig. 6.13), consisting of 1.1 million second-order isoparametric tetrahedrons, was generated with the average element size of 3.0 mm everywhere except for the welding beads (size of 2.0 mm).

The material properties (carbon steel) were assigned using the isotropic linear elastic constitutive model with Young's modulus of 200 GPa, Poisson's ratio of 0.29, yield strength of 204 MPa, and von Mises yielding criterion. The welding beads were assigned the same material properties as the rest of the model, which is a conservative assumption (actual welding beads are made of E60 electrode with yield strength of 330 MPa).

The part was modeled as a multi-body system with five separate objects. Bonded contact (as if objects were ideally glued together) with compatible mesh option (nodes of the objects are shared) was applied to the surfaces where the welding beads were in contact with connected objects. Direct contact between the parts (no penetration condition for touching faces) was not modeled. Welding beads were modeled as 10 mm single-side fillet edge welding beads.

Three loadcases were considered (see Fig. 6.14a-c) with different boundary conditions which replicate several scenarios of the loads from the dynamic simulations:

1. The part is fixed at the surface of the top middle hole. Vertical load of 90 kN is equally distributed over the surfaces of the four bottom holes;

2. Part is fixed at the surface of the top middle hole. Horizontal load of 13 kN and vertical load of 22.52 kN is applied to each surface of the four bottom holes. Load
vector is aligned outward and has an angle of 60° with horizon. The resultant force is vertical and equals to 90 kN;

(3) Part is fixed at the surfaces of all four bottom holes. Vertical force of 90 kN is applied to the surface of top middle hole.

The analysis (see Fig. 6.14d-f) shows that the loadcase 1 produced the worst-case conditions with the highest magnitude of stresses. It was found that there were about 0.5% of elements (by volume) with safety factor $S \leq 3.5$, and about 0.06% of elements with $S \leq 2.0$. Since this loading scenario represents the storm conditions (rare high-energy events) and the material of the part (carbon steel) has relatively high ductility, it was decided that this stress distribution is acceptable, and no design revision is necessary. Fig. 6.14g illustrates the distribution of stresses which are higher than $1/3.5$ of the yield strength.

### 6.5.3. Ballast lines hub plate

Finite element analysis was used to model the mechanical response to dynamic loads of the ballast lines hub plate using the quasi-static loadcases. The geometry was designed in the CAD software (SolidWorks), and the analysis was performed using the Simulation module of the software. The mesh, consisting of 1.4 million second-order isoparametric tetrahedrons, was generated with the average element size of 5.0 mm, minimum of 16 divisions per circle, and growth factor of 1.2. The connection edges (see Fig. 6.15) were meshed with the element size of 1.0 mm. The material properties (carbon steel) were assigned using the isotropic linear elastic constitutive model with Young's modulus of 200 GPa, Poisson's ratio of 0.29, yield strength of 204 MPa, and von Mises yielding criterion.

The part was modeled as a multi-body system with five separate objects. Bonded contact (as if objects were ideally glued together) with compatible mesh option (nodes of the objects are shared) was applied to the surfaces where the welding beads were in contact with connected objects. Direct contact between the parts (no penetration condition for touching faces) was not modeled. Welding beads were modeled as 10 mm single-side fillet edge welding beads.
Fig. 6.14. Boundary conditions (a-c) and the distribution of safety factor (d-f) for loadcases 1-3, correspondingly. (g) Isosurface of von Mises stresses higher than 58 MPa (1/3.5 of the yield strength) shown on the deformed shape of the plate (deformation scale 637:1) for loadcase 1.
Three loadcases were considered (see Fig. 6.16a-c) with different boundary conditions which replicate several scenarios of the loads from the dynamic simulations:

(1) Part is fixed at the surface of the top hole. Vertical load of 90 kN is equally distributed over the surfaces of the twelve bottom holes simulating contact load from the attached shackles;

(2) Part is fixed at the surface of the top hole. Horizontal load of 7.5 kN (normal to the surface) and vertical load of 7.5 kN is applied to each surface of the twelve bottom holes. The resultant force is vertical and equals to 90 kN;

(3) Part is fixed at the surface of the top hole. Horizontal load of 7.5 kN and vertical load of 7.5 kN is applied to each surface of the twelve bottom holes. The resultant force is vertical and equals to 90 kN.

The analysis (see Fig. 6.16d-f) shows that the loadcase 3 produced the worst-case conditions with the highest magnitude of stresses. It was found that there were about 1.0% of elements (by volume) with safety factor $S \leq 3.5$, and about 0.1% of elements with $S \leq 2.0$. Since this loading scenario represents the storm conditions (rare high-energy events) and the material of the part (carbon steel) has relatively high ductility, it was decided that this stress distribution is acceptable, and no design revision is necessary. Fig. 6.16g illustrates the distribution of stresses which are higher than $1/3.5$ of the yield strength.
Fig. 6.16. Boundary conditions (a-c) and the distribution of safety factor (d-f) for loadcases 1-3, correspondingly. (g) Isosurface of von Mises stresses higher than 58 MPa (1/3.5 of the yield strength) shown on the deformed shape of the plate (deformation scale 443:1) for loadcase 3.
6.5.4. Net chamber and attachments

The 10 m deep net chamber is fabricated from Br-1 wire, woven into chain-link mesh configuration, with a 4.0 mm wire diameter and a 40 mm bar length. The netting is suspended from the net pipe via individual “double loops” of brass wire (Fig. 6.9, details A, B), located every 150 mm along the pipe. The bottom rim is attached via a similar method. The fish cage is designed to support a net chamber of this material on the sides and bottom of the circular chamber. For the top panel, nylon netting is chosen as a cheaper solution, which also avoids accelerated corrosion concerns (splash zone corrosion when the system is floating on the surface).

The choice of net chamber attachment methodology was one of the most important steps in the design of this system. Several factors influenced the choice of a particular design of the net chamber attachments. First, it was important to design the attachments that provide sufficient strength to withstand the static and dynamic loads from the heavy netting. In addition to that, redundancy of the attachments was critical to ensure that in case of an attachment point failure, the whole system would not collapse. Another factor was the choice of net chamber attachment type (rigid, complaint or hybrid). The net assembly and attachment procedure was required to be straightforward to simplify cage system construction and in-situ maintenance. Finally, it was important to have the net constantly in tension to avoid excessive net wear (based on the previous experience with the chain-link mesh in offshore cages, see DeCew et al., 2010a).

In the selected configuration, the net is attached directly to a small diameter HDPE pipe located beneath the buoyancy pipes. Thus, copper netting is constantly submerged at least 0.5 m below the water surface and protected from accelerated corrosion in the splash zone. Net panels are outlined in 5 mm wire to reinforce the edges. The net is attached to the pipes with individual “double loops” as shown in Fig. 6.9. This attachment method provides an extremely tight connection to the top and bottom net pipes, even distribution of the loads around the cage circumferences, and redundancy in the event of a single connector failure.

Dynamic analysis described in Section 6.4 indicates that the net chamber can experience significant loads under the applied environmental conditions. A finite element analysis was
performed using a commercial finite element solver (MSC Marc/Mentat) to determine the critical loads that this specific mesh can withstand. Netting was oriented in the same way as in the service conditions: vertical axis was aligned with the picket direction. Top ends of the wires were fixed and the load was applied normally to the ends of the pickets on the bottom (Fig. 6.17a). The load was prescribed as the linearly increasing ramp with fixed stepping of 1.6 N. A sensitivity study was performed to investigate the effect of the number of simulated pickets (4, 6, 8) and their length (2–5 spiral revolutions) on the predicted yield strength of the mesh. An additional set of simulations was performed with one more constraint to restrict mesh shrinking in the transverse direction (Fig. 6.17b) to investigate the yield strength under this condition.

The netting geometry was constructed based on the actual picket geometrical parameters (see Fig. 5.8): width $W = 61\, \text{mm}$, pitch $P = 132\, \text{mm}$, wire diameter $d = 4.0\, \text{mm}$. The finite element mesh was generated using meshing module of CAD system (SolidWorks 2012) using the following parameters: average element size of $1.2\, \text{mm}$, mesh

![Fig. 6.17. Geometry and boundary conditions: (a) without and (b) with transverse constraint.](image)
type set as second-order isoparametric tetrahedrons. For the geometry shown in Fig. 6.17, the mesh consisted of 184,000 elements. The net panel was modeled as an assembly of individual pickets with touching contact taken into account. Surface contact modeling was necessary to maintain integrity of the mesh and to obtain accurate predictions for the stresses at the connection points. Contact between the surfaces of the individual pickets was modeled as no penetration (touching) contact. To optimize the contact modeling, only small areas around the intersection of the pickets were defined as contact areas while all other elements were excluded from contact analysis.

The material properties (alloy Br-1) were assigned using the elasticity data from Table 5.1. Plasticity was not considered because the critical load was defined as the onset of yielding based on the values of Von Mises equivalent stress.

The critical load with the onset of yielding was defined as the load, at which the yield stress is exceeded in more than 0.01% of elements by volume. This criterion was selected instead of the criterion for a single element with the highest stress to reduce the dependence of the level of finite element discretization. The analysis (Fig. 6.18) showed that the critical load is around 89 N and 58 N per picket for the cases with and without the transverse constraint, correspondingly. Comparing these predictions with the simulations and experimental testing of an individual picket (see Section 5.2.2), it can be seen that these values are within the same load range. However, these loads are lower than the expected

Fig. 6.18. Strength analysis of the chain-link mesh. (a) Joints are modeled as solid elements with contact regions shown in color. (b) Distribution of the equivalent stress at one of the joints.
service loads, and therefore the stress concentrations at the joints can exceed the allowable limits. To address this concern, additional load bearing members had to be incorporated for absorption of snap loads. Two solutions were considered:

- additional straight copper alloy wire woven through the netting and secured to the net pipes. However, a large number of additional wires (~200) was required to provide sufficient increase in strength;
- utilization of resin impregnated or coated steel cables adjacent to the net. As few as 18 cables were needed to protect the net chamber during the storm.

First method has an advantage of material compatibility, while the second one allows for a more straightforward fabrication. Due to the limited supply of the copper alloy wire, the second option was employed. To insure that the cables absorb the net loading, their length was specified slightly shorter than the height of the net chamber deformed due to its self-weight.

Finally, it was important to isolate the net from coming in contact with the galvanized steel brackets. To achieve this, a protective boot was designed to fit over the steel net supports, and held in place by the net pipes.

6.5.5. Airlift–ballast assembly

To control position of the fish cage in the water column, an airlift–ballast assembly is used. This airlift device controls submergence through buoyancy adjustments. It consists of a steel and concrete framework with an inflatable airbag. The lift bag is placed inside the ballast structure with an air hose leading up to the surface. The airlift system is designed to be always negatively buoyant to prevent damage to the fish cage by the ascent of the airlift. The airlift-ballast assembly is supported below the cage by twelve ballast bridle lines. These lines are shackled into a ballast connection plate, designed to ease the installation and removal of each shackle. They are isolated from each other to limit the wear. In the event one of the lines fails, the remaining lines can operate as expected and allow the failed member to be replaced in-situ. A single ballast line runs from the connection plate to the airlift-ballast assembly. The ballast weight and bridle arrangement provide a dynamic
restoring force that helps maintain volumetric stability when the two rims above (top superstructure and bottom rim) move relative to each other in waves, currents or during surfacing/submerging operations.

When the cage is operated at the surface, the bag is inflated, offsetting the weight of the ballast (Fig. 6.19). To submerge the cage, the bag is deflated (via hose at the surface) reducing the system's reserve buoyancy. The cage stops its descent when the ballast weight reaches the seafloor. In the event the ballast becomes stuck in the seafloor sediment, a back-up pendant line can be used to free the system.

A lift bag can be operated via an HDPE hose that runs along the cage's exterior. Back up valves and break points in the line at several points along the length of the cage are incorporated to allow replacement of the hose sections if necessary. The hose at the surface is outfitted with two valves (one redundant) to insure that air does not escape during normal operations.

Finite element analysis was used to model the mechanical response to dynamic loads of the airlift-ballast frame using the quasi-static loadcases. The geometry was designed in the CAD software (SolidWorks), and the analysis was performed using the Simulation module of the software. Due to symmetry only one quarter of the frame was analyzed (see Fig. 6.20).

![Fig. 6.19. The fish cage in the surface (left) and submerged (right) positions.](image)
With the geometry consisting mostly from plates and only few 3D objects (pad-eyes), most of the frame components were modeled using thin and thick shell elements, except for the pad-eyes (total of three) which were modeled with solid elements. A mixed mesh with 170,000 elements was generated (see Fig. 6.21), consisting of second-order triangles (plates, tubes) and tetrahedrons (pad-eyes). The following meshing parameters were used: average element size of 10.0 mm, minimum of 8 divisions per circle, and growth factor of 1.2. The material properties (carbon steel) were assigned using the isotropic linear elastic constitutive model with Young's modulus of 200 GPa, Poisson's ratio of 0.29, yield strength of 204 MPa, and von Mises yielding criterion.

Fig. 6.20. The frame geometry: full frame (left), and one quarter used in analysis (right).

Fig. 6.21. Finite element mesh of the frame.
The frame was modeled as a multi-body system with thirty separate objects:

- 9 I-beams (6mm thickness, thin shells), three faces have thickness of 3 mm due to symmetry of the model cut
- 1 large plate (6mm thickness, thin shell)
- 8 strip gussets (6mm thickness, thin shells)
- 1 box channel (6mm thickness, thin shells)
- 2 C-channels (6mm thickness, thin shells)
- 1 L-channel (6mm thickness, thin shells)
- 4 triangular gussets (10mm thickness, thick shells)
- 1 cap (20mm thickness, thick shell)
- 3 pad-eyes (solid elements)

Bonded contact (as if objects were ideally glued together) with compatible mesh option (nodes of the objects are shared) was applied to the connections of: I-beams to the large plate, pad-eyes to the large plate, L-channel to the box channel. All other connections were modeled as single-side 6 mm fillet edge weld connectors made of E60 electrode (total of 43 edge welds). Direct contact between the parts (no penetration condition for touching faces) was not modeled.

The boundary conditions were selected based on the orientation and magnitude of the loads from the dynamic analysis. Symmetry constraints were applied to the faces and edges that belong to the symmetry planes. Because the concrete blocks (walls around the frame) were not included in the analysis, appropriate boundary conditions were placed on the I-beams at corresponding locations. Horizontal load of 13 kN and vertical load of 22.5 kN was applied to the surface of the top pad-eye. Load vector is aligned inward to the center of the frame and has an angle of 60° with the horizon. The resultant force in a full frame is vertical and equals to 90 kN.

Analysis (see Fig. 6.22a-g) shows that in general the airlift-ballast frame satisfies the safety factor requirements, however 12 out of 43 welds require additional review (or increase in weld size) to ensure sufficient strength. Appropriate modifications were added to the drawings to specify the required weld sizes.
Fig. 6.22. Finite element analysis of the airlift-ballast frame: (a) boundary conditions; (b) distribution of the safety factor; (c–d) distribution of von Mises stresses shown on the deformed mesh (deformation scale 432:1); (e–f) weld check plot showing welds with sufficient safety factor in green, and the welds that do not have sufficient strength in red; (g) example of the weld bead plot showing the calculated minimum weld size as a function of weld length. (h) Distribution of the von Mises stresses on the deformed (scale of 320:1) base plate subjected to the buoyancy force of 55 kN.
Additional simulation (see Fig. 6.22h) was performed to ensure that the base plate (with I-beams beneath it) has sufficient strength to withstand buoyancy forces (a total of 55 kN applied to the four pad-eyes) when the airbag is inflated. It was found that the base plate needed slight design revision to satisfy the strength requirements.

In addition to the selected design, several other submersion technologies and techniques were investigated for providing submergence control, including utilization of various rim configurations as variable buoyancy chambers, integration of a variable buoyancy central spar inside the cage, and utilization of a separate airlift and a ballast weight below the cage. The described configuration with airlift-ballast assembly was chosen for the following reasons:

- Eliminates the possibility of losing buoyancy of the main cage frame in the event of a valve failure (if cage frame was used as a variable buoyancy chamber).
- The airlift-ballast assembly is located on the central axis of the system helping insure stable surfacing and submerging operations.
- The system is easy to use and can be submerged with small infrastructure and few personnel.
- The net pen can be utilized without the airlift-ballast assembly for surface operations.
- The cage system requires limited diving operations because filling and emptying the variable buoyancy member are performed at surface.
- During the fish grow-out, the assembly can be removed, repaired, replaced, etc.
- The variable buoyancy member does not intake or exhaust water. The outside water pressure collapses the bag when air is released (at the surface). Pressurized surface air expands the bag, restoring buoyancy.

However, the choice of an external ballast system limits the net pen reserve buoyancy as compared to traditional surface cage systems or systems with an internal ballast system (such as the one in which main rims operate as variable buoyancy members). The reserve buoyancy of the system is linked to the variability in buoyancy associated with the airlift-ballast assembly. The more reserve buoyancy is required, the larger variable buoyancy member is needed, thus driving up the weight of the ballast. It is important to note that
mooring systems should be compatible with the design of fish cage and choice of the submergence control device (e.g. airlift).

With the fish cage and mooring system analyses complete, the design was presented for review with the industry personnel. The design was finalized, full engineering documentation was generated, and later used for fabrication, assembly and deployment of two identical systems at different locations in the South Pacific.

6.6. Conclusions and observations from the deployment

Engineering procedures for design of a submersible fish cage with copper netting should include the following major steps: establishment of the design constraints, development, and analysis of the conceptual design, review with construction and operational personnel, verification of the final design, and development of the construction and deployment procedures.

To illustrate this approach, design steps for the development of a submersible fish cage utilizing copper alloy net chamber are presented. To address the concerns associated with the introduction of a new netting material, robust net attachment methodologies were developed. In addition, the employed brackets were modified from the standard aquaculture bracket designs, providing not only adequate structural support to the system but also the opportunity to convert a standard gravity fish cage with nylon netting to the one with copper mesh. The airlift-ballast assembly was integrated into the design to protect the cage system from toxic algae blooms and heavy storms by submerging the cage below the surface.

To facilitate easy integration into the local aquaculture farming community, the cage system was designed for construction and deployment with small infrastructure. Two offshore aquaculture systems were fabricated and deployed in the South Pacific. One system (see Fig. 6.23) is presently secured in a near-shore fish farm and stocked with
Atlantic salmon for a trial grow-out. The second system is deployed in an exposed site having current velocities approaching 1 m/s and wave heights of 5 m. Both cage systems are being monitored for structural and operational issues that may develop, and have not shown significant degradation over the two-year period.
Chapter 7. Conclusions

Successful utilization of high performance materials, such as copper-based alloys, for marine applications requires a comprehensive engineering approach, which combines evaluation of their seawater performance (biofouling and corrosion) and mechanical behavior, as well as hydrodynamic analysis and design procedures for the components made of these materials. In this dissertation, all of these aspects are addressed through the combination of experimental testing and numerical modeling.

Mesh geometry of the major types of copper alloy nets currently used in the marine aquaculture was analyzed, and formulae for the solidity and strand length were derived and validated. Experimentally obtained normal drag coefficients of copper alloy net panels were documented and compared to the published data on polymer nets. It is shown that copper nets exhibit significantly lower resistance to normal currents, which corresponds to lower values of normal drag coefficient. None of the available analytical models can be directly applied to predict drag forces on copper alloy nets. It is suggested that the solidity alone cannot be used as a sufficient parameter to predict drag coefficients of nets made of different materials. Proper description of the drag characteristics of fishnets should take into account such parameters as mesh geometry, flexibility and roughness of strands.

The corrosion and fouling rates of copper alloys were obtained from a one-year field testing at the Portsmouth Harbor (USA). The 3-month corrosion rates for untensioned specimens were on average 2.4 times higher than the rates from 12-month testing. In the tensioned deployment, 12-month corrosion rates were 1.4 times higher than the rates from untensioned testing. The biofouling resistance was excellent for all but one alloy, which exhibited heavy fouling by barnacles. Low biofouling resistance of this alloy is attributed to the low Cu-ion release rate (associated with low corrosion rate) and presence of Aluminum in its composition. Studies of the localized corrosion did not reveal significant localized damage due to a one-year seawater exposure. Significant variations in seasonal
corrosion rates were observed, however, no correlation was found with the changes in physical/chemical environmental parameters. It is suggested that studies of microfouling can provide insight into this phenomenon. To investigate the effects of stray electrical currents on the corrosion rates, a low cost three-axis stray electric current monitoring device was designed. It is shown that DC currents should not affect the observed corrosion rates by more than 25%, and that effect of AC currents can be considered negligible.

The effect of one-year seawater exposure on the mechanical properties of copper alloy was analyzed through the uniaxial tension tests. No significant changes in stiffness, strength or ductility were observed. It is shown that the stress-strain data (adjusted for the reduction in thickness) of the virgin specimens provides a good estimate of the mechanical behavior after one year of seawater exposure.

Experimentally obtained plastic behavior of plates and wires made from alloy of the same composition show a significantly different response. We attribute this to the differences in the manufacturing process (effects of heat treatment and cold working). The stiffness and strength of chain-link pickets was characterized through the tension testing. The observed elasto-plastic response of these components was accurately reproduced in a developed numerical model. It was observed that the experimentally obtained force-displacement behavior of a chain-link net panel under transverse tensile loading can be approximated as quasi-linear up to the initiation of pickets' failure. Testing of the double-loop connectors showed that these components fail by untwisting of the wires instead of necking. This behavior is attributed to high ductility of the material.

Using the collected data on corrosion, biofouling and mechanical performance, modifications to the design and fabrication procedures were proposed for engineering of the offshore fish farms utilizing copper alloy netting. These procedures were illustrated on a commercial size gravity-type offshore fish cage, which was designed and successfully deployed in the Pacific Ocean near Isla Italia (Patagonia, Chile). It is shown that the existing fish cage systems can be converted for use with copper alloy netting in a straightforward way.
One of the major conclusions with respect to the design and service life predictions of the copper alloy components in marine environment is that for the engineering analysis purposes, it is possible to decouple the complicated environmental effects into the separate analyses (corrosion, mechanics, hydrodynamics). This approach significantly simplifies the engineering procedure for developing new systems with copper alloys, as shown on the example of a marine aquaculture fish cage. However, the tribological interaction between the pickets (wear and fretting corrosion of chain-link nets) was not considered and requires further studies.
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