



# Acquisition Directorate

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## Research & Development Center

Report No. CG-D-02-15

# Ballast Water Treatment Corrosion Scoping Study Interim Report

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# Ballast Water Treatment Corrosion Scoping Study

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16. Abstract (MAXIMUM 200 WORDS) The major emphasis of ballast water treatment research has been on the performance of treatment on marine organisms. Most treatment systems use active substances (chemicals) to disinfect ballast water. A potential side-effect of these disinfectants is an increase in corrosion rates. The US Coast Guard needs to understand the implications of ballast water treatment on corrosion of vessel's materials. This report represents Phase 1: Corrosion Scoping Study of the project. It contains a literature review that identifies both existing treatment technologies and available corrosion data.					
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### EXECUTIVE SUMMARY

To date, the major emphasis of Ballast Water Treatment (BWT) investigations has been the systems' effects on organisms in tanks prior to discharge. One of the risks of treating ballast water is the potential to accelerate corrosion in the ballast tanks and piping. Although most commercially-available BWT systems currently use active substances to treat ballast water, corrosion tests are infrequently performed as part of a BWT system's overall assessment. If tests are included, the methods used are most often measurements of linear polarization resistance or redox-potential. Such measurements can only be indicative and are seldom conclusive.

For the maritime industry, corrosion and corrosion protection is a considerable cost element in the operation of a vessel. Consequently, any technology which significantly accelerates corrosion or can reduce the efficacy of presently applied protective corrosion measures are likely to be discarded, even if the ballast water treatment performance is good. This may result in an increased risk of non-indigenous species introductions from the discharge of untreated ballast water and the potential of an economic hardship for vessels that purchase the corrosive treatment systems.

The U.S. Coast Guard (USCG) needs to understand how ballast water treatments affect the corrosion rates in ballast tanks and associated piping. This project will provide USCG with the necessary information and recommendations on how to assess corrosion acceptability as part of type-approval. The project is divided into two phases: Phase 1: Corrosion Scoping Study and Phase 2: Corrosion Rate Assessment.

This report represents Phase 1: Corrosion Scoping Study. It includes a literature review of the corrosion behavior of shipboard materials normally exposed to ballast water and an assessment of how different ballast water treatment processes may affect corrosion rates of these materials. The study found that there is significant variability in the results of corrosion testing among treatment manufacturers, many of whom conducted their own tests.

Due to the variability of test results among the limited studies that have assessed treatment effects on ballast tank corrosion, it is recommended that laboratory testing be conducted in both freshwater and saltwater environments. The tests should evaluate the corrosion effects of several ballast water treatment processes on several different materials. The laboratory tests should simulate chlorination, deoxygenation, and chlorine dioxide disinfection processes. Results should include both visual inspections and weight loss analysis.

It is also recommended that shipboard testing be conducted on two difference vessel platforms. One platform should be the uncoated ballast tanks of a "Laker" that operates in the Great Lakes and the other platform should be the coated ballast tanks of a "Salty" that operates in seawater.



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### LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ABS	American Bureau of Shipping
ANS	Aquatic Nuisance Species
ASTM	American Society of Testing and Materials
BW	Ballast Water
BWMS	Ballast Water Management System
CDA	Copper Development Association
cfu	Colony Forming Unit
CP	Cathodic Protection
Cu-Ni	Copper Nickel
Cu-Zn	Copper Zinc
ECG	Electrolytic Chlorine Generator
EPDM	Ethylene Propylene Diene Monomer
Fe-Mn	Iron-Manganese
FKAA	Florida Keys Aqueduct Authority
ft/s	Feet per second
GESAMP	Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection
gpm	Gallons per minute
IMO	International Maritime Organization
LPR	Linear Polarization Resistance
m <sup>3</sup>	Cubic Meter
MCA	Multiple Crevice Assembly
MEPC	Marine Environmental Protection Committee
g L <sup>-1</sup>	Milligram per Liter
MIPR	Military Interdepartmental Purchase Request
mL	Milliliter
mm	Millimeter
NACE	National Association of Corrosion Engineers
NANPCA	Nonindigenous Aquatic Nuisance Prevention and Control Act
NaCl	Sodium Chloride
NIOZ	Nederlands Instituut voor Onderzoek der Zee
NISA	National Invasive Species Act
NRLKW	Naval Research Laboratory Key West



**LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS (CONTINUED)**

ppm	Parts per million
PTFE	Polytetrafluoroethylene
R <sub>p</sub>	Polarization Resistance
STDN	Severn Trent De Nora
STEP	Shipboard Technology Evaluation Program
TRC	Total Residual Chlorine
TRO	Total Residual Oxidant
USCG	United States Coast Guard
UV	Ultraviolet
µm	Micrometer
VOS	Venturi Oxygen Stripping™



**1 INTRODUCTION**

The transfer of non-indigenous species into coastal waters by way of ballast water is an ongoing difficulty, both domestically and internationally. Ballast water discharged from ships is one of the vectors by which aquatic nuisance species (ANS) have been introduced. In response to the concerns of ANS introductions, Congress enacted the Nonindigenous Aquatic Nuisance Prevention and Control Act of 1990 (NANPCA). NANPCA, which was reauthorized by National Invasive Species Act of 1996 (NISA), was intended to identify and implement ballast water management practices that would reduce introductions of ANS into U.S. waters. Under both laws, Congress directed the United States Coast Guard (USCG) to establish regulations and guidelines for ships to manage their ballast water.

In August 2009, the Coast Guard proposed to amend its ballast water management regulations by establishing a two-phase discharge standard that will define the maximum concentration of living organisms a ship may discharge. The proposed Phase I standard will require all large ships operating in U.S. waters to install a Coast Guard-approved ballast water management system (BWMS) that will disinfect the water before discharge. The proposed Phase II standard is much more stringent than Phase I and is expected to be enacted sometime in the future. Phase I and Phase II standards are referenced in Table 1.

Table 1. Proposed Phase I & II ballast water discharge standard table extracted from the USCG Office of Environmental Standards. (USCG Office of Environmental Standards, 2009)

Organism Size	> 50µm*	> 10µm & ≤ 50µm	≤ 10µm	Pathogens and Indicators		
				Toxicogenic <i>V. cholerae</i> O1 & O139	<i>E. coli</i>	Intestinal enterococci
Phase One	< 10 / m <sup>3</sup>	< 10 / mL	N/A	< 1 cfu / 100 mL	< 250 cfu / 100 mL	< 100 cfu / 100 mL
Phase Two	< 1 per 100 m <sup>3</sup>	< 1 per 100 mL	< 1,000 bacteria & 10,000 viruses per 100 mL	< 1 cfu / 100 mL	< 126 cfu / 100 mL	< 33 cfu / 100 mL

\* µm: micrometer, a measurement of length, is equal to 1/1,000 of a millimeter or about 4/100,000 of one inch. [Colony forming unit (cfu), micron (µm), milliliter (mL), cubic meter (m<sup>3</sup>)]

An international response has also been implemented to address ANS. The International Maritime Organization (IMO), which is the United Nations agency responsible for the safety and security of shipping and prevention of marine pollution, has been at the head of the international effort to address the transfer of ANS. Starting in 1991, the IMO adopted a series of resolutions containing recommended practices to help prevent the introduction of ANS by ballast water. The current resolution was adopted in 1997 and contains guidelines calling for mid-ocean ballast water exchange and other ballast water management practices. Following adoption of that resolution in 1997, a ballast water working group regularly convened as part of the meetings of IMO’s Marine Environment Protection Committee (MEPC), with a charge of developing legally binding requirements for a ballast water management treaty. During the Diplomatic Conference held at the IMO in February 2004 the text of a ballast water management Convention was adopted, titled “International Convention for the Control and Management of Ships’ Ballast Water and Sediments”, 2004 (hereinafter referred to as “the Ballast Water (BW) Treaty”). The BW Treaty will not enter into force until it has been ratified by at least 30 countries

representing not less than 35% of the gross tonnage of the world's merchant shipping. The US is not presently a signatory and the treaty has not entered into force internationally. Information on the status of IMO Conventions (International Maritime Organization, 2011) indicates that as of 14 October 2010, 27 countries have ratified the Convention, representing 25.32% of the world merchant fleet tonnage. The IMO Convention requirements for ballast water discharge are the same as the USCG Phase I Discharge Standards presented in Table 1.

Most of the BW treatment technologies have been developed by industrial and municipal water treatment manufacturers. To date, the studies of BWMSs have focused on treatment effects on organisms prior to discharge. One of the risks of treating ballast water is the potential to increase the rate of corrosion in the ballast tanks and piping system which can affect ship safety and normal maintenance procedures. For the maritime industry, corrosion and corrosion protection is a considerable cost in the normal operation of a vessel. As a consequence, any BWMS that increases corrosion rates may not be installed even if the treatment performance is satisfactory. As such, the USCG needs to understand how the use of BWMSs affects the corrosion rates of ballast tanks and piping systems.

USCG Research and Development Center (RDC) has funded Naval Research Laboratory Key West (NRLKW) through a Military Interdepartmental Purchase Request ((MIPR) HSCG32-11-X-ROOO05) to investigate the corrosion effects caused by ballast water management systems.

## 2 TYPES OF CORROSION

It is generally accepted that the marine environment is one of the most corrosive naturally occurring environments, due to its salty air, saline seawater, dew, condensation, and localized high temperatures. The common corrosion process occurring in ship ballast tanks is electrolytic and is caused by local electric potential differences between anodic and cathodic sites on steel surfaces.

Corrosion is prevalent in several areas and in different forms throughout a ship. The types of corrosion found in the marine environment are as follows:

- Uniform corrosion
- Crevice corrosion
- Microbiological corrosion
- Hydrogen embrittlement
- Pitting corrosion
- Erosion corrosion
- Galvanic corrosion
- High temperature corrosion
- Stress corrosion cracking
- Stress assisted corrosion
- Stray current corrosion
- Waterline corrosion
- Weld corrosion
- Coating related corrosion

## Ballast Water Treatment Corrosion Scoping Study

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- Corrosion under lagging
- Intercooler and heat exchanger corrosion

Types of corrosion most often encountered inside ballast tanks are detailed below.

### 2.1 Uniform Corrosion

Uniform corrosion (Figure 1), also referred to as general corrosion, is normally associated with the rusting of steel and is one of the most common forms of corrosive attacks on ships, including surfaces of ballast tanks.



Figure 1. Uniform corrosion observed on a steel piping system exposed to seawater. (Lomas & Callow, 2009)



### 2.2 Crevice Corrosion

Crevice corrosion (Figure 2) is localized attack of a metal that occurs at a narrow opening or space caused by contact with another material. This type of corrosion is generally associated with the presence of small volumes of stagnant water beneath deposits and seals, in crevices, or where nuts and rivet heads are fastened. Crevice corrosion is normally observed in areas of ballast tanks with stagnant water, such as lap joints, or in areas where the coating has disbonded.



Figure 2. Example of crevice corrosion that developed under a pipe hanger due to stagnant water. (Lomas & Callow, 2009)

### 2.3 Pitting Corrosion

Pitting corrosion (Figure 3) is a form of extremely localized corrosion that leads to the creation of small holes or “pits” in the metal. The driving force for pitting corrosion is a lack of oxygen around a small area. This area becomes anodic, while the areas of excess oxygen become cathodic leading to very localized corrosion. The corrosion area tends to tunnel into the mass of the metal with limited diffusion of ions additionally increasing the localized lack of oxygen. This kind of corrosion is normally observed with little loss of material on the surface. Metals that are susceptible to uniform corrosion normally do not undergo pitting. For example, regular carbon steel will corrode uniformly, whereas stainless steel will pit. Pitting tends to occur in stagnant water and in the presence of chloride ions that can significantly increase the conditions for formation and growth of pits.



Figure 3. Pitting corrosion observed on a flat wall (Lomas & Callow, 2009).

### 3 BALLAST WATER TREATMENT TECHNOLOGIES

Currently, there are two basic types of process technologies used in ballast water treatment: solid-liquid separation and disinfection. Solid-liquid separation is the separation of suspended particles and organisms from the ballast water. This is typically accomplished by surface filtration, with filter pore size of 30-50  $\mu\text{m}$ . Disinfection removes and/or inactivates organisms through chemical treatment (chlorination, electrochlorination, ozonation, chlorine dioxide, peracetic acid, hydrogen peroxide, and menadione), or physical inactivation (ultraviolet radiation, deoxygenation, gas injection, ultrasonic treatment, and cavitation). Most treatment systems use a combination of solid-liquid separation and disinfection.

According to the 2010 Lloyd's Report (Lloyd's Register, 2010), there are currently 47 different ballast water management systems either commercially available or projected to be commercially available by 2011. The breakdown of disinfection processes by percentage is as follows:

- Electrochlorination/Electrolysis—28%
- Ultraviolet Radiation (UV)—26%
- Ozonation—14%
- Deoxygenation—10%
- Chlorine Based—6%
- Ultrasound—6%
- Other—10%



This study focuses on three disinfection processes of ballast water treatment: electrochlorination, deoxygenation, and chlorine dioxide disinfection. These technologies are reviewed below.

### 3.1 Electrochlorination/Electrolysis

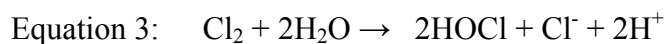
Electrochlorination/Electrolysis systems make up the largest share of ballast water management systems that treat using disinfection. Electrolytic disinfection systems typically generate sodium hypochlorite (NaOCl) by passing a direct electrical current between an anode and a cathode that are in water containing sodium chloride (NaCl). In an electrochlorination system, the anode and cathode system is called the electrolytic cell. The primary reaction is represented by Equation 1. Equations 1 through 9 were provided by Severn Trent De Nora (STDN). (Severn Trent De Nora, 2010)



Chlorine ( $\text{Cl}_2$ ) is produced at the anode (Equation 2).



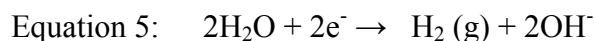
The chlorine is broken down in solution with water ( $\text{H}_2\text{O}$ ) to form hypochlorous acid (HOCl) (Equation 3).



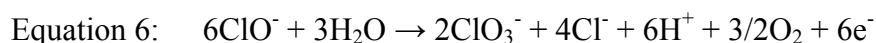
The hypochlorous acid (HOCl) dissociates to hypochlorite ( $\text{ClO}^-$ ) in the bulk solution (Equation 4).



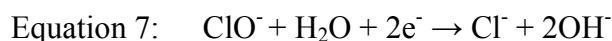
At the cathode, hydrogen ( $\text{H}_2$ ) gas and the hydroxide ion ( $\text{OH}^-$ ) are formed (Equation 5).



Because the anode and cathode compartments are not normally segregated (un-separated electrolytic cells), the compounds and ions created at the anode and cathode locations are free to react in the solution to form the respective end products. This includes side reactions which lead to the decomposition of hypochlorite ( $\text{ClO}^-$ ) to chloride ( $\text{Cl}^-$ ) and chlorate ( $\text{ClO}_3^-$ ) and oxygen ( $\text{O}_2$ ) (Equation 6).



Also, hypochlorite can be decomposed at the cathode to chloride (Equation 7).



Initially, a portion of the produced chlorine is consumed as a result of substances, such as inorganic material and metal ions that convert the chlorine to forms that have no oxidizing power (Droste, 1997). These side reactions (for example, Equation 6 and Equation 7) can reduce the disinfection efficiency. The portion of the chlorine without oxidizing power is referred to as the chlorine demand. The remaining chlorine, *active or residual chlorine*, is the concentration of chlorine available for disinfection (Lewis, 1966). This is typically the measurement taken to determine whether the ballast water has enough disinfectant to treat the water. The residual chlorine is comprised of the combined chlorine, chlorine that has reacted with ammonia or other nitrogenous compounds, and the free chlorine,

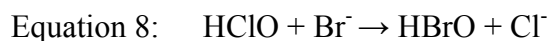




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hypochlorous, and hypochlorite. Though both hypochlorous and hypochlorite disinfect, hypochlorous acid is a stronger disinfectant than the hypochlorite ion (Droste, 1997).

Seawater is comprised of approximately 60 parts per million (ppm) of bromine. The bromine reacts with the chlorine and dislocates it. This changes the above chemical products to form hypobromous acid (HBrO) and hypobromite (BrO<sup>-</sup>) as shown in Equation 8 and Equation 9. Hypobromous becomes the biocide that eliminates the larger size class organisms, and hypobromite the disinfectant to eliminate the bacteria. These two reactions are unique to seawater systems.



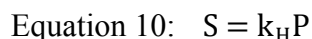
The residual oxidants, such as chlorine and bromine oxidants, produced by electrochlorination refer to the disinfecting concentration in seawater. The residual concentration dosage of several commercially available ballast water treatment systems is presented in Table 2.

Table 2. Electrolytic chlorine generation (ECG) systems and dosage rates. (Lloyd's Register, 2010)

Type of Disinfection	Company Model	Concentration (Dose) of Treatment	Source of Information
Electrolytic Chlorine Generator (sodium hypochlorite)	Lloyd's Register	"Most chlorination systems are applying a dose in the region of 2 mg L <sup>-1</sup> residual chlorine	Lloyd's Report "Ballast Water Treatment Technology"—February 2010
Electrolytic Chlorine Generator (sodium hypochlorite)	Electriclor	8 mg L <sup>-1</sup> in a 6 hour period with 1 mg L <sup>-1</sup> of residual chlorine	Electriclor "Ballast Water Treatment" (Electriclor, 2002)
Filtration + Electrolytic Chlorine Generation (Sodium Hypochlorite)	STDN BalPure™	12 mg L <sup>-1</sup> maximum. Normal dosing of 6-8 mg L <sup>-1</sup> with a 1-2 mg L <sup>-1</sup> residual chlorine	STDN "Electrochemical Disinfection Capabilities Statement of Qualifications" (Severn Trent De Nora, 2008)
Filtration + Electrolytic Chlorine Generation (Sodium Hypochlorite)	Siemens SiCURE™	6 mg L <sup>-1</sup> residual chlorine.	Siemens Water Technology "Frequently Asked Questions-SiCURE™ Ballast Water Management System
Filtration + Electrolytic Chlorine Generation (Sodium Hypochlorite)	RWO—CleanBallast	2.5 mg L <sup>-1</sup> maximum with normal operation at 2 mg L <sup>-1</sup> residual chlorine	Response from email received 4/1/2011

### 3.2 Deoxygenation

Many microorganisms found in ballast water thrive in oxygenated environments. Reported values for surface dissolved oxygen concentrations of seawater and freshwater are 7 to 10 mg L<sup>-1</sup> (Pickard & Emery, 1990), (Dexter & Culberson, 1980) and 11 mg L<sup>-1</sup> (Makarewicz, 1991), respectively. The concentration of dissolved oxygen in ballast water is proportional to the partial pressure of the oxygen gas in contact with the ballast water. This relationship is provided by Henry's Law according to Equation 10.



## Ballast Water Treatment Corrosion Scoping Study

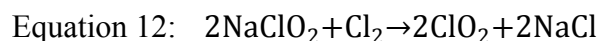
S is the solubility of the gas in the solution,  $k_H$  is Henry's Law constant for the gas in a specified solution, and P is the partial pressure of the gas. Deoxygenation, reduction in the dissolved oxygen concentration, of ballast water can be achieved by reducing the partial pressure of the oxygen in contact with the water. This is commonly accomplished by bubbling an inert gas such as nitrogen into the water or creating a vacuum over the water. Since deoxygenation limits the concentration of molecular oxygen in the ballast water, many of the microorganisms are asphyxiated. Dissolved oxygen levels achieved by two commercially available deoxygenation ballast water treatment systems are given in Table 3.

Table 3. Deoxygenation systems and achievable oxygen concentration. (Lloyd's Register, 2010)

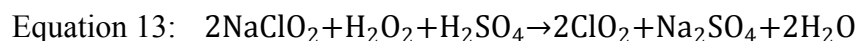
Type of Disinfection	Company-Model	Concentration (dissolved O <sub>2</sub> in treated ballast water)	Source of Information
Deoxygenation + Cavitation	Coldharbour Marine	<0.2 mg L <sup>-1</sup>	Response from e-mail inquiry received 5/25/2011.
Deoxygenation + cavitation	NEI Treatment Systems LLC	<1 mg L <sup>-1</sup>	Presentation from NEI Treatment Systems "Can Ballast Water Treatment Affect Ship's Life Cycle Cost?" (Ito, 2008)

### 3.3 Chlorine Dioxide Disinfection

Another method of ballast water treatment is disinfecting with chlorine dioxide (ClO<sub>2</sub>). Chlorine dioxide is unstable when stored as a gas so it is typically generated onsite and injected into the ballast water stream. There are various ways to produce chlorine dioxide, but in disinfection applications, the fundamental reactions are sodium chlorite (NaClO<sub>2</sub>) reacting with an acid, as in Equation 11, or with chlorine gas, as in Equation 12.



There is currently one company, Ecochlor Inc., using chlorine dioxide as a ballast water treatment. Ecochlor Inc. first pumps water through a Venturi device, which draws a vacuum in the mixing chamber. Once the vacuum is drawn, sodium chlorite and hydrogen peroxide (Purate®), along with sulfuric acid are injected into the mixing chamber. The formation of chlorine dioxide is illustrated in Equation 13 (ClO<sub>2</sub> Technology, 2011).



The chlorine dioxide fills the mixing chamber, and is injected into the ballast water line. According to the Land-Based Testing Report on the Ecochlor System performed by Nederlands Instituut voor Onderzoek der Zee (NIOZ) (Veldhuis, 2008), ballast water treated with a 4 mg L<sup>-1</sup> dose of chlorine dioxide after a coarse mechanical filtration step (40 micron filter) meets the IMO D-2 standard. Ecochlor Inc. recommends a chlorine dioxide dose of 5 mg L<sup>-2(1)</sup>.

<sup>1</sup> The 5 mg L<sup>-1</sup> dose recommendation was provided in e-mail correspondence from a representative of Ecochlor, Inc received on May 26, 2011.

### 4 SCOPING STUDY RESULTS

NRLKW has completed a literature review to identify available corrosion data related to BWMS. Findings are detailed below.

#### 4.1 Corrosion Due to Chlorinated Seawater

A corrosion test in natural seawater was conducted for STDN by GL Noble Denton in 2010 and 2011 (G & I, 2011). GL Noble Denton is an international independent testing service that conducted corrosion testing on four substrates: structural steel EN 10025 S275JR, 90/10 Cu-Ni alloy Copper Development Association (CDA)706, Naval Brass CDA464, and structural steel EN 10025 S275JR coated with Intershield 300 (which is a ballast tank coating supplied by International Paint).

The test included immersion exposure tests carried out using ASTM G 31 guidance for both fully immersed and partially immersed conditions in three seawater test environments (natural seawater, natural seawater dosed to 2 mg L<sup>-1</sup> free chlorine, and natural seawater dosed to 8 mg L<sup>-1</sup> free chlorine). The tests were conducted for 6 months at room temperature. Metallic specimens were evaluated for weight loss and pitting corrosion. In addition, the copper alloy tests were supplemented by crevice corrosion test using fully immersed multiple crevice assembly (MCA) specimens and electrochemical cyclic potentiodynamic polarization tests. The coated panels included partial immersion tests with the panels scribed on one side. The coated panels were evaluated for degree of blistering, cracking, disbondment, and delamination (flaking of the coating). Pull-off adhesion tests were carried out as well.

According to the report, the coated steel panels had no significant difference between the three test environments in terms of degree of blistering, rusting, cracking, and disbondment. The degree of delamination after 6 months exposure indicated no significant difference between the three environments. There was no significant difference for the adhesion pull-off test.

The Cu-Ni alloy CDA 706 and Naval Brass CDA 464 specimens exhibited similar mass-loss derived corrosion rates of less than 0.01 mm/year for all three test environments. The extent of corrosion of the area covered by the MCA crevice washer for the Naval Brass CDA 464 was greater in seawater with 2 mg L<sup>-1</sup> and 8 mg L<sup>-1</sup> free chlorine added when compared with natural seawater alone.

There was increased corrosion found for the EN 10025 S275JR structural steel when exposed to natural seawater with 8 mg L<sup>-1</sup> free chlorine. According to the report, after 6 months of exposure the mean-loss derived corrosion rates were 0.059 mm/year in natural seawater, 0.077 mm/year in seawater with 2 mg L<sup>-1</sup> free chlorine, and 0.086 mm/year in seawater with 8 mg L<sup>-1</sup> free chlorine. The report then compared these values with the published corrosion rates found in the “Corrosion Handbook” (Kreysa & R, 1992) and “The Corrosion of Metals in Marine Environments” (Revie, 2000). The corrosion rates observed in the books ranged from 0.053 to 0.188 mm/year, so this study concluded that “any acceleration of corrosion due to the presence of free chlorine was likely to be of little significance in ballast tanks” (G & I, 2011).

Thomas et al. (Thomas, Lucas, Peterson, & Christian, 1988) investigated the effect of chlorinated seawater on the corrosion behavior of eight alloys common to seawater cooling systems (Table 4). Three identical test loops were used to expose coupons to natural and halogenated seawater (1 and 4 mg L<sup>-1</sup> total oxidant) for six months to one year. Halogenation of the seawater was achieved by electrolytic

## Ballast Water Treatment Corrosion Scoping Study

chlorination with concentric platinized titanium flow-through electrodes. Samples of each alloy (five replicates) were mounted in 0.1 m/s flumes. Mass-loss derived corrosion rates were provided. Table 4 presents the corrosion rates of the eight alloys in natural seawater and in chlorinated seawater (1mg L<sup>-1</sup> and 4 mg L<sup>-1</sup>).

Table 4. Corrosion rates of several alloys in natural and chlorinated seawater.\*

	Corrosion Rate ( 10 <sup>-3</sup> mm/year)		
	Natural Seawater	Chlorinated Seawater: 1 mg L <sup>-1</sup>	Chlorinated Seawater: 4 mg L <sup>-1</sup>
<b>C70600</b> (Cu-Ni 90/10)	5	11	13
<b>C71500</b> (Cu-Ni 70/30)	5	5	16
<b>N06625</b> (Inconel 625)	1	3	6
<b>N04400</b> (Monel 400)	27	7	24
<b>N05500</b> (Monel 500)	6	5	18
<b>R50400</b> (Ti CP-2)	0	0	0
<b>R56400</b> (Ti 6-4)	0	0	0
<b>S30400</b> (CRES 304)	4	3	13

\*Adapted from (Thomas, Lucas, Peterson, & Christian, 1988)

Concentrations refer to total oxidant levels.

Corrosion rate values of 0 mm/year denote no measureable corrosion attack.

No corrosion attack was measured on Ti CP-2 or Ti-6-4 any of the three conditions. Cu-Ni 90/10 and Inconel 625 experienced increased corrosion rate with increased chlorination levels. The authors described the exposure to 1 mg L<sup>-1</sup> chlorinated seawater as not influencing the corrosion rates of Cu-Ni 70/30, Monel 500, and CRES 304. However, the corrosion rates of all three alloys tripled in the 4 mg L<sup>-1</sup> electrolyte. The corrosion rate of Monel 400 was higher in untreated seawater, 0.027 mm/year, than in the 1 mg L<sup>-1</sup> chlorinated seawater, ~0.007 mm/year. The corrosion rates in untreated seawater and 4 mg L<sup>-1</sup> treated seawater were similar.

No corrosion attack was visually observed on Ti CP-2 or Ti-6-4 for any of the three conditions. Cu-Ni 90/10 and 70/30 alloys were susceptible to crevice corrosion, but the authors concluded it was independent of halogenation. Uniform etching was observed on Inconel 625 coupons at 4 mg L<sup>-1</sup>. The Monel 400 and 500 coupons experienced localized corrosion at all conditions. Chlorination caused pitting corrosion of CRES 304.

Anderson and Richards (Anderson & Richards, 1966) examined the effect of chlorinated seawater on steel, Cu-Ni 90/10, Cu-Ni 70/30, admiralty brass, and aluminum brass test spools. The testing apparatus consisted of eight individual units with each unit including a 6-inch diameter, 15-foot long rubber-lined pipe. The desired mixture of seawater and hypochlorite solution was fed into the rubber-lined pipes. After mixing, the solution was directed to small diameter pipe lines and then into overflow weir boxes, which housed the testing spools. Experiments were 59 to 187 days in duration with a 10-gallon per minute (gpm) flow through the weir boxes and seawater temperatures ranging from 60 to 76 °F.

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Table 5 provides the corrosion rates for steel, Cu-Ni 90/10, Cu-Ni 70/30, admiralty brass, and aluminum brass when exposed to residual chlorine concentrations of 0 (untreated seawater), 0.1, 0.25, and 0.5 mg L<sup>-1</sup>. The authors concluded that chlorinated seawater has little effect on the corrosion rate of steel at a low flow rate of 10-gpm. There was little difference between the corrosion rates of Cu-Ni 90/10 in natural seawater, 0.03 mm/year, in 0.1 mg L<sup>-1</sup> treatment, 0.02 mm/year, and in 0.5 mg L<sup>-1</sup> treatment, 0.04 mm/year. The highest corrosion rate of Cu-Ni 90/10 (0.07 mm/year) was observed after exposure to the 0.25 mg L<sup>-1</sup> treated seawater. Cu-Ni 70/30 was generally not affected by the chlorination treatments. For admiralty brass, all of the corrosion rates in the various residual chlorine concentrations (0.1 – 0.12 mm/year) were higher than the rate in the untreated seawater (0.05 mm/year). The highest corrosion rate of aluminum brass was 0.10 mm/year in the 0.1 mg L<sup>-1</sup> treated seawater, and its lowest corrosion rate, 0.02 mm/year, was in the untreated seawater.

Table 5. Corrosion rates of selected marine alloys in untreated seawater and seawater with 0, 0.1, 0.25, and 0.50 mg L<sup>-1</sup> residual chlorine. Adapted from (Anderson, D.B. and Richards, B.J. 1966).

	Corrosion Rate (mm/year)			
	Natural Seawater	Chlorinated Seawater: 0.1 mg L <sup>-1</sup>	Chlorinated Seawater: 0.25 mg L <sup>-1</sup>	Chlorinated Seawater: 0.50 mg L <sup>-1</sup>
Steel	0.25	0.30	0.23	0.20
70/30 Cu-Ni	0.02	-	0.02	0.01
90/10 Cu-Ni	0.03	0.02	0.07	0.04
Admiralty Brass	0.05	0.12	0.10	0.10
Aluminum Brass	0.02	0.10	0.06	0.07

Corrosion rates from in the 0.1 mg L<sup>-1</sup> treated seawater were obtained from one experiment.

Corrosion rate of 70/30 Cu-Ni in the 0.5 mg L<sup>-1</sup> treated was obtained from two experiments

All other experiments consisted of at least three replicates.

In 1944, the Texas Division of Dow Chemical Company established a station to test the effects of chlorination and velocity on the corrosion rates of steel pipe sections. Steel pipe sections were investigated in six pipe runs (Volkening, 1950). Five of the pipe runs were injected with chlorine solutions with residual chlorine concentrations of 0, 0.5, 1, 2, and 4 mg L<sup>-1</sup>. Each pipe run contained ¾", 1", 1 ½", and 2" diameter sections giving water velocities of 1.0, 1.65, 3.9, and 6.4 feet per second (ft/s). A sixth pipe run was tested using chlorinated plant seawater with a residual chlorine concentration range of 0.0 to 0.3 mg L<sup>-1</sup>. The testing was for 14 months, and both weight loss measurements and pit analyses were performed on the pipe sections. Results from the pipe runs with controlled chloride concentrations are presented in Table 6.

In general, the corrosion rate and maximum pit depth increased as the residual chloride concentration increased with the trends being more pronounced at the two higher velocities (6.4 and 3.9 ft/s). The highest corrosion rate, 1.00 mm/year, was observed at a velocity of 3.9 ft/s and chlorine concentration of 4 mg L<sup>-1</sup>. For a velocity of 6.4 ft/s, the corrosion rate of steel was 0.18 mm/year in untreated seawater and 0.88 mm/year in 2 and 4 mg L<sup>-1</sup> treated seawater. The maximum pit depths at a velocity of 6.4 ft/s for steel were 1.47 mm in untreated seawater and 2.87 mm in 2 and 4 mg L<sup>-1</sup> treated seawater. At the lower velocities, the corrosion rate and pit depth dependence on chloride concentration was more erratic. For instance, the corrosion rate of the steel exposed to untreated seawater flowing at 1 ft/s, 0.27 mm/year, was higher than the corrosion rates of steel exposed to chlorinated seawater flowing at the same velocity.

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Table 6. Corrosion rates and maximum pit depths of steel pipe sections seawater of varying chlorine concentrations and at various velocities.\*

Pipe Run Number	Pipe Diameter (in)	Velocity ft/s	Residual Chlorine (mg L <sup>-1</sup> )	Corrosion Rate (mm/year)	Percent Pipe Wall Penetration	Maximum Pit Depth (mm)
1	3/4	6.4	0	0.18	51.4	1.47
	1	3.9	0	0.29	23.3	0.79
	1 1/2	1.65	0	0.36	57.2	2.11
	2	1.0	0	0.27	46.7	1.83
2	3/4	6.4	4	0.88	100.0	2.87
	1	3.9	4	1.00	79.0	2.67
	1 1/2	1.65	4	0.50	96.6	3.56
	2	1.0	4	0.17	31.8	1.24
3	3/4	6.4	2	0.88	100.0	2.87
	1	3.9	2	0.51	100.0	3.38
	1 1/2	1.65	2	0.44	73.2	2.69
	2	1.0	2	0.20	36.4	1.42
4	3/4	6.4	1	0.78	70.7	2.03
	1	3.9	1	0.52	54.1	1.83
	1 1/2	1.65	1	0.17	29.7	1.09
	2	1.0	1	0.14	35.1	1.37
5	3/4	6.4	0.5	0.60	73.5	2.11
	1	3.9	0.5	0.49	41.4	1.40
	1 1/2	1.65	0.5	0.27	82.8	3.05
	2	1.0	0.5	0.14	29.2	1.14

\*Table adapted from (Volkening, 1950).

### 4.1.1 Commercial Chlorination Studies

#### 4.1.1.1 Siemens SiCURE™ System Corrosion Study

The Siemens SiCURE™ is a combination physical separation (filtration) and electrolytic chlorine generation. This BWMS produces sodium hypochlorite to a maximum dosage of 6 mg L<sup>-1</sup>. Siemens developed a corrosion test program based on recommendations for corrosion testing by the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) published in the Marine Environmental Pollution Council (MEPC) document 59/2/16 in April 2009 (Siemens Water Technology, 2009).

The goal of this test program was to evaluate the possible corrosion effects caused by the Siemens SiCURE™ system on different materials that may be used in a ship's ballast tanks or piping systems. The test included the following materials:

- Carbon steel coupons coated with a ballast tank epoxy coating
- Uncoated carbon steel coupons
- Stainless steel 316L
- Brass (CuZn20Al2)
- Copper Nickel alloy ((Cu-Ni)10 Iron-Manganese (Fe-Mn))
- Ethylene Propylene Diene Monomer (EPDM)
- Polytetrafluoroethylene (PTFE)

## Ballast Water Treatment Corrosion Scoping Study

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The corrosion study was completed over a 6-month period using natural seawater. The first set of samples was treated with sodium hypochlorite with an average Total Residual Chlorine (TRC) level of  $6 \text{ mg L}^{-1}$ . TRC is defined as the amount of remaining total chlorine in the water after the initial reactions had been completed. Chlorine was added as a standard dilution of bulk sodium hypochlorite. The second set of samples was exposed to untreated seawater. All samples were fully immersed in water. The coated samples were inspected monthly for blistering and a final inspection to look at blistering, rusting, cracking, flaking delamination and coating adhesion was conducted at the end of the six month test.

Testing of the uncoated samples was completed in accordance with the crevice corrosion testing guidelines in ASTM G78 and the immersion corrosion guidelines in ASTM G31. These samples were evaluated for corrosion rate measurement using mass loss on a monthly basis. Visual inspection of crevice formations was carried out with photography and the depth of each crevice location was measured. Pitting was also evaluated at the end of the 6-month period using metallographic examination. Short term polarization tests were carried out on all of the uncoated metal samples using an Autolab Potentiostat (PGSTAT302N) according to ASTM G61. Unfortunately, this report did not provide results.

Since results were not provided for this test, a different source was sought for results. According to the SiCURE Frequently Asked Questions web page (Siemens Water Technology, 2011), Siemens performed corrosion testing in cooperation with Thyssen Krupp and International Paint under supervision from Germanischer Lloyd. A 6-month test comparing natural seawater and water treated at  $6 \text{ mg L}^{-1}$  TRC concentration was conducted on a variety of alloys, ballast tank coatings, and gasket materials. The results showed that the use of hypochlorite resulted in increased corrosion rates for uncoated carbon steel as compared to the specimens exposed to natural seawater. Brass, copper nickel, rubber and polymer based gasket samples were unaffected by hypochlorite. Crevice corrosion was actually reduced by exposure to hypochlorite and there was no effect on the ballast tank coating (Intershield 300-International Paint).

### 4.1.1.2 *Techcross Electro-Cleen™ System*

The Techcross Electro-Cleen™ system is an electrochlorination (no filtration) ballast water treatment system. This company has several images posted on their website (TECHCROSS, 2011) of coated panels that were exposed to saltwater (25% NaCl) treated to a TRO of 25 ppm compared to panels sitting in just saltwater (25% NaCl) over a 6-month period. Half of the panels were scribed into the panels. According to the text provided in this web page, “exposure to hypochlorite at a concentration of  $10 \text{ mg L}^{-1}$  TRC will not significantly increase ballast tank corrosion.”



### 4.2 Corrosion Due to Deoxygenated Seawater

Tamburri et al. (Tamburri, K., & Matsudo, 2002) conducted an 18-month shipboard study on a 150,000 ton coal/ore carrier to examine the effect of deoxygenation on the corrosion behavior of steel panels. Steel test plates were placed at the bottom of two separate 908 m<sup>3</sup> ballast tanks. The control was allowed to operate in standard ballast tank conditions. The other tank was bubbled with nitrogen under a constant pressure. The oxygen level in the control tank was approximately 20.9% while the level in the deoxygenated tank dropped to ~0.5% ( $\leq 0.2 \text{ mg L}^{-1}$ ). In general, the corrosion rate of the steel test plates (0.06 mm/year) in the deoxygenated tank was lower than that of plates in the control ballast tank (0.47 mm/year). Rust levels were considerably lower on the deoxygenated samples compared to the control samples (Matsuda, Kobayashi, Miyuki, & Yosida, 1999). Obvious signs of hydrogen sulfide due to microbial production were not observed.

Lee et al. (Lee J. S., Ray, Lemieux, Tamburri, & Little, 2004) monitored uncoated carbon steel (C1020) coupons for 140 days in natural seawater and deoxygenated seawater chambers (Figure 4). The deoxygenated chamber was maintained with a blanket of inert gas (5% CO<sub>2</sub>, 10% H<sub>2</sub>, and the balance N<sub>2</sub>). Coupons were oriented at four different heights in the chamber – three rows vertically and one row horizontally to simulate the sides and bottom of a ballast tank, respectively. Then open-circuit potentials of the coupons were continuously monitored, and the Linear Polarization Resistance (LPR) technique was performed every 30 to 90 days to determine the polarization resistance ( $R_p$ ), which can be used to assess a material's ability to resist general corrosion. The inverse of  $R_p$ ,  $1/R_p$ , was used as a measure of the instantaneous corrosion rate.

Figure 4 illustrates that after 23 days the instantaneous corrosion rates were low for coupons in both untreated and deoxygenated environments. With extended exposure, the coupons in the deoxygenated case exhibited higher corrosion rates than those in the control. For both conditions, samples mounted at the bottom of the chambers experienced more aggressive corrosion. The average weight loss after 124 days for coupons in the untreated (naturally oxygenated) case was 11.8 mg for the vertically mounted coupons and 22.5 mg for the horizontally mounted (bottom) coupons. The average weight loss after 139 days in the deoxygenated case was 29.7 mg for the vertically mounted coupons and 52.1 mg for the horizontally mounted coupons. Coupons exposed to seawater in the untreated condition developed an adherent iron oxide on the surface while coupons exposed to the deoxygenated condition developed a layer of non-adherent sulfur-rich microorganisms in corrosion products.





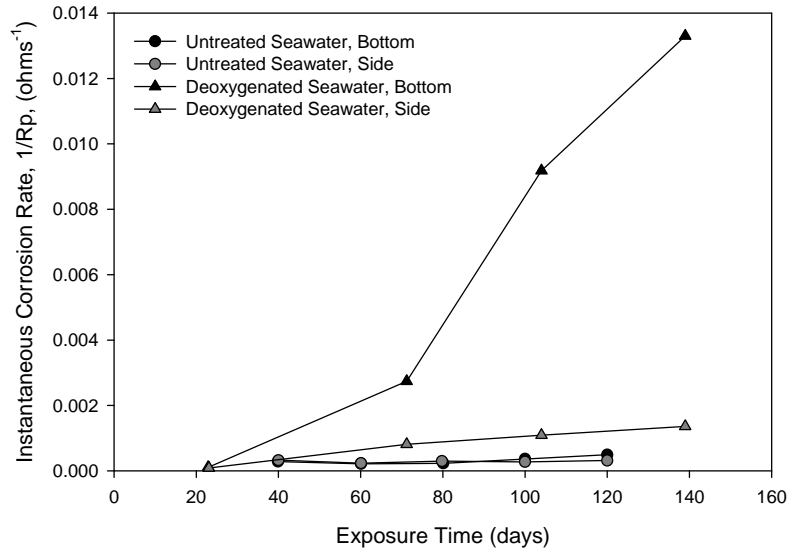


Figure 4. Instantaneous corrosion rates of carbon steel coupons exposed to naturally oxygenated (untreated) and deoxygenated seawater. Adapted and re-plotted from (Lee J. S., Ray, Lemieux, Tamburri, & Little, 2004).

A similar study from Lee and co-authors (Lee J. S., Ray, Little, & Lemieux, 2005) examined the influence of deoxygenation on the corrosion behavior of uncoated 1020 carbon steel. As mentioned in the previous paragraph, coupons were oriented at four different heights to simulate the sides and bottom of a ballast tank. Samples were mounted in three chambers corresponding to the following fill/drain cycles: [1] alternating natural seawater and air, [2] alternating deoxygenated seawater and air, and [3] alternating deoxygenated seawater and inert gas. An in-line injection of a mixture of CO<sub>2</sub> and N<sub>2</sub> deoxygenated the seawater (< 0.1 ppm). This mixture of inert gas was used in the fill/drain cycle. The LPR technique was conducted every 30 to 90 days to determine the instantaneous corrosion rates. Coupons mounted horizontally at the bottom of the deoxygenated seawater/air chamber had the highest corrosion rates. The coupons exposed to the deoxygenated seawater and inert gas exhibited lower instantaneous corrosion rates, but the inadvertent introduction of oxygen (gasket failure) resulted in an immediate increase in corrosion rate. The authors concluded that going from a hypoxic environment to an oxygenated environment resulted in an increase in the corrosion rate and severity of corrosion.

### 4.2.1 Commercial Deoxygenation Study: NEI VOS™ System

The NEI Venturi Oxygen Stripping™ (VOS™) technology is a deoxygenation system that creates a low-oxygen condition in a ship's ballast tanks using inert gases. This company has a link on their website related to corrosion control. According to text provided on this website (NEI Marine, 2011), low-oxygen inert gas fills ballast tanks during the ballast discharge such that oxygen levels are below 4.0%, and the corrosion rates are decreased by as much as 84%.

In 2008, Masahiko Ito presented information at a National Association of Corrosion Engineers (NACE) international conference (Ito, 2008) regarding corrosion studies conducted on the Motor Tanker *TI Africa* in 2007 with a reduced oxygen atmosphere (4% O<sub>2</sub>). This vessel was an oil tanker that had the tank "inerted" during off-load of crude; therefore, the oxygen levels were reduced. The survey conducted on this vessel indicated that the anodes which were designed to be reduced to 10% after 5 years had actually remained intact (95%) in the reduced oxygen environment. Coating breakdown was

also substantially reduced and very little rust staining was observed. It was trying to correlate the reduced oxygen in this vessel to the VOST™ oxygen stripping system which is designed to produce an atmosphere of 0.1% O<sub>2</sub>.

### 4.3 Corrosion Due to Chlorine Dioxide Treatment

Singh et al. (Singh, 2002) examined the electrochemical polarization and immersion behaviors of 316L, 317L, 2205, and 254SMO stainless steels in acidic chlorine dioxide solutions. To achieve target chloride concentrations, varying amounts of chlorine dioxide gas was dissolved in distilled water. Immersion experiments were performed on samples fitted with serrated washers. Solutions, which were based off the solution composition in bleach plant washers, had chlorine dioxide concentrations of 50 and 100 mg L<sup>-1</sup> and chloride ion concentrations of 500 to 3000 mg L<sup>-1</sup>. The pH values of the solutions were either 3 or 5.

As determined by potentiodynamic experiments, 316L and 317L were more vulnerable to localized corrosion than 2205 and 254 in the tested solutions. The experiments revealed 316 L and 317 L alloys exhibited lower pitting breakdown potentials than 2205 and 254SMO. Therefore, 316 L and 317 L were more vulnerable to pitting corrosion than 2205 and 254SMO in the tested solutions. In solutions with 50 mg L<sup>-1</sup> ClO<sub>2</sub> and 500 mg L<sup>-1</sup> Cl<sup>-</sup>, an increase from a pH of 3 to 5 resulted in higher pitting potentials for 2205 and 254SMO. The higher pitting potentials at a pH of 5 indicate the alloys were more resistant to pitting corrosion in less acidic environments.

Six-month immersion experiments were performed in four solutions with pH values of 3 and 5, ClO<sub>2</sub> concentrations of 50 and 100 mg L<sup>-1</sup>, and Cl<sup>-</sup> concentrations of 1000 mg L<sup>-1</sup> (Table 7). Stainless steel alloys 316L and 317L were susceptible to crevice attack in all solutions with 316L experiencing the more aggressive crevice attack. The 2645MO alloy was resistant to crevice corrosion in all solutions. Crevice attack was only observed on 2205 in the solution with a pH of 3 and ClO<sub>2</sub> concentration of 50 mg L<sup>-1</sup>.

Table 7. Mass-loss derived corrosion rates for stainless steels exposed to various ClO<sub>2</sub> solutions.\*

	Alloy	Corrosion Rate (10 <sup>-3</sup> mm/year)
pH = 3 ClO <sub>2</sub> = 50 ppm Cl <sup>-</sup> = 1000 ppm	316L	5.84
	317L	1.5
	2205	1.27
	254SMO	0.254
pH = 5 ClO <sub>2</sub> = 50 ppm Cl <sup>-</sup> = 1000 ppm	316L	5.08
	317L	2.03
	2205	1.27
	254SMO	0.0254
pH = 3 ClO <sub>2</sub> = 100 ppm Cl <sup>-</sup> = 1000 ppm	316L	10.1
	317L	11.4
	2205	0.762
	254SMO	0.508
pH = 5 ClO <sub>2</sub> = 100 ppm Cl <sup>-</sup> = 1000 ppm	316L	5.84
	317L	5.58
	2205	0.508
	254SMO	0.508

\*Adapted from (Singh, 2002). pH measurements were within ± 0.10  
ClO<sub>2</sub> measurements were within ± 10 ppm. Cl<sup>-</sup> measurements ± 20 ppm



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At a pH of 3, mass-loss derived corrosion rates increased with an increase in ClO<sub>2</sub> concentration for 316L ( $5.84 \times 10^{-3}$  to  $1.01 \times 10^{-2}$  mm/year) and for 317L ( $1.5 \times 10^{-3}$  to  $1.14 \times 10^{-2}$  mm/year). The 2205 alloy's corrosion rate decreased from  $1.27 \times 10^{-3}$  to  $7.62 \times 10^{-4}$  mm/year with an increase in ClO<sub>2</sub> concentration. An increase in corrosion rate from  $2.54 \times 10^{-4}$  to  $5.08 \times 10^{-4}$  mm/year was measured for 2545MO with the increase in ClO<sub>2</sub>.

At a pH of 5, the increase in ClO<sub>2</sub> (50 to 100 mg L<sup>-1</sup>) slightly increased the corrosion rates of 316L, from  $5.08 \times 10^{-3}$  to  $5.84 \times 10^{-3}$  mm/year, and 317L, from  $2.03 \times 10^{-3}$  to  $5.58 \times 10^{-3}$  mm/year. The corrosion rate decreased for 2205 with increasing ClO<sub>2</sub> changing from  $1.27 \times 10^{-3}$  to  $5.08 \times 10^{-4}$  mm/year. With the increase in ClO<sub>2</sub> concentration, the corrosion rate of 2545MO increased from  $2.54 \times 10^{-5}$  to  $5.08 \times 10^{-4}$  mm/year. In general, 316L and 317L were most vulnerable to corrosion attack due to increases in ClO<sub>2</sub> concentrations

### 4.4 Corrosion Assessments in the Great Lakes Fleet

An American Bureau of Shipping (ABS) surveyor out of Marinette, WI was contacted regarding surveys that are conducted for vessels operating in the Great Lakes. The surveyor indicated that none of the vessels he has inspected have had a coating system. ABS is required to perform inspections of all ballast tanks every 5 years. During a normal tank inspection, the surveyor will climb into all of the tanks and perform a visual inspection using a flashlight and a chipping hammer. Generally, steel wastage allowance in the 25% range is allowed, but for some vessels only 10% wastage is allowed. Any areas where wastage appears to be too high will be documented, and then the ship-owner will be instructed to perform an ultrasonic thickness test on the area to determine the exact amount of corrosion damage.

The surveyor indicated that ballast tanks are constructed of carbon steel. Ordinary strength ABS shipbuilding steel comes in a number of grades: A, B, D, E, DC, and CS and some higher strength steels: AH32, DH32, EH32, AH36, DH36, and EH36. He has seen mostly A36 or AH36 steels with some B or D steels on occasion. All piping on the vessels he has surveyed is carbon steel piping and all fittings are welded. Valves are either cast steel or cast iron, and use flanges to fit into the piping system. Gaskets between the flanges are typically composite fiber-type gaskets.

During corrosion assessments, general corrosion is normally observed within the tanks. The higher mechanical stress areas normally experience a higher corrosion rate, and pitting is frequently observed; sometimes localized deeper pitting is observed. He did not indicate any correlation between higher corrosion rates and the water interface; rather, he indicated corrosion rates are higher in higher mechanical stress areas. Galvanic corrosion was not observed.

The surveyor has observed cathodic protection (CP) systems within several ballast tanks. Typically he sees zinc anodes within the tanks, although he has also seen aluminium anodes. Anodes are not required by ABS in freshwater ships; rather, the ship-owner can decide to install anodes within the ballast tanks. The surveyor indicated that the location and number of anodes is not carefully calculated. Finally, this surveyor was not aware of any ballast water treatment systems that are currently installed in the Great Lakes.



**4.5 Corrosion due to Chlorinated Freshwater**

A study published in 1994, examines the possibility of using stainless steel in piping systems in potable water plants (Table 8). Carbon steel (1010), cast iron, and 304 and 316 stainless steels were exposed to four concentrations of chlorinated fresh water (Tuthill, 1994). Three of the four exposure racks from International Nickel Company were in Lake Ontario locations and the fourth in an inland freshwater location. Chlorine residual concentrations were 0, 0.8 to 1.0, 2, and 3 to 5 mg L<sup>-1</sup>.

General corrosion rates for 1010 carbon steel and cast iron increased with chlorine residual concentration. At 0 mg L<sup>-1</sup> chlorine residual (untreated fresh water), the corrosion rate was 0.036 mm/year for carbon steel and was 0.043 mm/year for cast iron. At a 2-mg L<sup>-1</sup> residual concentration, the corrosion rates were at least twice the untreated rates. Carbon steel had a corrosion rate of 0.27 mm/year at the 3- to 5-mg L<sup>-1</sup> chlorine residual level. Cast iron was not tested at the highest chlorine residual level.

Table 8. Corrosion rates of carbon steel and cast iron and maximum pit and crevice depths of stainless steels in unchlorinated and chlorinated fresh water. (Tuthill, 1994)

Chlorine Residual (mgL <sup>-1</sup> )	Corrosion Rates (mm/year)		Maximum Pit Depth Attack (mm)				Maximum Crevice Depth Attack (mm)			
	Carbon Steel	Cast Iron	304SS	316SS	304SS, Sensitized	304SS, Sensitized	304SS	316SS	304SS, Sensitized	304SS, Sensitized
0	0.04	0.04	0	0	0	0	0	0	<0.03	0
0.8 - 1.0	0.06	0.08	0	0	0	0	0	0	<0.03	<0.03
2	0.09	0.09	0	0	30	0	0	0	0.89	0.03
3 - 5	0.27	NT	<0.03	0	NT	NT	0.10 – 0.36	0.03 – 0.13	NT	NT

Table adapted from (Tuthill, 1994).

Since stainless steels are vulnerable to localized corrosion, their corrosion was assessed in terms of maximum depth attack. The only measurable pitting and crevice attack for Type 304 stainless steel was a maximum pit depth of less 0.03 mm and a maximum crevice depths of 0.10 to 0.36 mm both occurring at the 3 to 5 mg L<sup>-1</sup> chlorine residual range. Type 316 had no resolvable pitting attack for any of the four of the chlorination levels, and crevice attack (0.03 to 0.13 mm) was only observed at the highest chlorine range.

Sensitized 304 and 316 stainless steels were also exposed to chlorine residual concentrations of 0, 0.8 to 1.0, and 2 mg L<sup>-1</sup>. Pitting attack on sensitized 304 stainless steel occurred at the 2 mg L<sup>-1</sup> chlorine condition with a maximum pit depth of 0.76 mm. Crevice attack was detected at 0 and 0.8 to 1.0 mg L<sup>-1</sup> (depths less than 0.3 mm) and at 2 mg L<sup>-1</sup> (maximum depth of 0.89 mm). No pitting attack was observed for sensitized 316 stainless steel. Crevice attack of sensitized 316 stainless steel occurred at 0.8 to 1.0 mg L<sup>-1</sup> chlorine (< 0.03 mm) and 2 mg L<sup>-1</sup> chlorine (0.03 mm).

### 5 SUMMARY AND CONCLUSIONS

#### 5.1 Scoping Study

The reviewed literature reports do not show a clear relationship between chlorination treatments of quiescent seawater and the corrosion rates of carbon steels (Anderson & Richards, 1966) (Volkening, 1950). The corrosion behaviors of brass and Cu-Ni 90/10 were detrimentally affected when exposed to seawater treated with chlorination (Thomas, Lucas, Peterson, & Christian, 1988) (Anderson & Richards, 1966). Tuthill (Tuthill, 1994) found chlorination treatments to fresh water increased the corrosion rates of carbon steel and cast iron.

Tamburri et al. (Tamburri, K., & Matsudo, 2002) reported corrosion rates of carbon steel were lower in deoxygenation of seawater than in untreated seawater. Contrastingly, Lee et al. (Lee J. S., Ray, Lemieux, Tamburri, & Little, 2004) illustrated higher corrosion rates for carbon steel when exposed to deoxygenated seawater compared to untreated seawater. A subsequent report from Lee et al. (Lee J. S., Ray, Little, & Lemieux, 2005) illustrated a reduction of carbon steel corrosion rates due to deoxygenation of seawater was possible; but if any oxygen was introduced into the environment, the corrosion rates could increase significantly.

Singh and coauthors (Singh, 2002) reported that increasing the concentration of chlorine dioxide in distilled water increased the corrosion rates of 316L, 317L, and 254SMO. Corrosion loss was more significant for 316L and 317L. Corrosion rates of 2205 decreased with increasing chlorine dioxide concentrations. Pitting vulnerability of 316L, 317L, 254SMO, and 2205 increased with increased chlorine dioxide concentrations. Pitting was more aggressive for 316L and 317L.

#### 5.2 Commercial Studies

There have been limited studies conducted on the effects of corrosion that may be caused by ballast water managements systems on normal ballast tank and piping materials. Several studies have been conducted at the bequest of ballast water manufacturers. Some of these studies have been conducted at independent test laboratories. Overall, the results are highly variable and often conflict with similar studies.

The results of the Siemens SiCURE™ test showed that the use of hypochlorite resulted in increased corrosion rates for uncoated carbon steel as compared to the specimens exposed to natural seawater. Brass, copper nickel, rubber and polymer based gasket samples were unaffected by hypochlorite. Results of the STDN BalPure™ test indicated coated steel panels had no significant difference between the three test environments (natural seawater, natural seawater dosed to 2 mg L<sup>-1</sup> free chlorine, and natural seawater dosed to 8 mg L<sup>-1</sup> free chlorine) in terms of degree of blistering, rusting, cracking, delamination and flaking. STDN's test found that crevice corrosion was greater in seawater with 2 mg L<sup>-1</sup> and 8 mg L<sup>-1</sup> free chlorine added when compared with natural seawater alone for the area covered by the MCA crevice washer for the Naval Brass CDA 464. They also noted an increase in corrosion found for the EN 10025 S275JR structural steel when exposed to natural seawater with 8 mg L<sup>-1</sup> free chlorine. Techcross claims exposure to hypochlorite at a concentration of 10 mg L<sup>-1</sup> TRC will not significantly increase ballast tank corrosion." NEI's test indicated anode degradation and coating degradation were reduced, and there was very little rust staining observed in a low oxygen environment.

### 6 RECOMMENDATIONS

Due to the variability of test results among the limited studies that have assessed treatment effects on ballast tank corrosion, it is recommended that laboratory testing be conducted in both freshwater and saltwater environments. The tests should evaluate the corrosion effects of several ballast water treatment processes on several different materials. The laboratory tests should simulate chlorination, deoxygenation, and chlorine dioxide disinfection. Results should include both visual inspections and weight loss analysis.

It is also recommended that shipboard testing be conducted on two different vessel platforms. One platform should be the uncoated ballast tanks of a “Laker” that operates in the Great Lakes and the other platform should be the coated ballast tanks of a “Salty” that operates in seawater.

#### 6.1 Phase 2: Laboratory Testing

NRLKW has proposed the following test matrices for the laboratory assessment of the selected ballast water disinfection processes.

##### 6.1.1 Laboratory Test Matrices

The laboratory testing will be divided into two matrices: Marine Test and Freshwater Test. The objective of the Marine Test will be to characterize the corrosion behavior associated with ballast water treatments on ballast tank and piping alloys common to marine vessels while the Freshwater Test will aim to characterize the corrosion behavior associated with ballast tank and piping alloys typical of freshwater vessels. The treatments that will be applied to natural seawater (Marine Test) and freshwater (Freshwater Test) will simulate chlorination, deoxygenation, and chlorine dioxide disinfection. All testing will be conducted at NRLKW. Natural, unfiltered seawater will be supplied for seawater testing; freshwater will be supplied from Florida Keys Aqueduct Authority FKAA. The chlorinated exposure tanks will be dosed to 10 mg L<sup>-1</sup> total residual oxidant (TRO). Reduced oxygen exposure tanks will be deoxygenated with inert gas to achieve a dissolved oxygen concentration of 0.2 mg L<sup>-1</sup>. The chlorine dioxide disinfected tanks will be dosed to 5 mg L<sup>-1</sup>.

Table 9 and 10 provide the test matrices for the Marine and Freshwater Tests, respectively. With regards to the Marine Test, seven types of specimens will be exposed to seawater and the three variations of treated seawater as well as untreated seawater. Uncoated and coated carbon steels are generally in ballast and holding tanks. Coated carbon steel specimens with scribes will serve to simulate coating damage. The scribed specimens with CP will be included since ballast tanks are cathodically protected for corrosion control. Cu-Ni and brass alloys are common materials for piping and fittings. The Freshwater Test only contains six types of specimens; coated specimens were excluded from this test given that ballast tanks in freshwater vessels are not coated. The specimens will be configured in the tank at three different heights. Exposure tanks will simulate ballast operations by filling and draining weekly for a period of 90 days such that the lower specimens experience constant immersion, the middle row will experience alternate immersion, and the top row will experience high humidity with no immersion. Specimens will be visually evaluated periodically for corrosion damage and weight loss analysis will be performed to quantify corrosion rates.



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Table 9. Marine test matrix.

	Uncoated Carbon Steel	Brass	Copper-Nickel	PTFE with Silica Fibers (Garlock FAWN GYLON® 3500)	Coated Carbon Steel	Coated Steel with scribe	Coated Carbon Steel with Scribe, Cathodically Protected
<b>Tank 1: Natural Seawater</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 2: Chlorinated Seawater</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 3: Deoxygenated Seawater</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 4: Chlorine Dioxide in Seawater</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Total spec. per Tank</b>	63						

Carbon steel to be coated with Intershield 300.

Table 10. Freshwater test matrix.

	Uncoated Carbon Steel	Cast Iron	Brass	Copper-Nickel	PTFE with Silica Fibers (Garlock FAWN GYLON® 3500)	Carbon Steel, Cathodically Protected
<b>Tank 1: Fresh Water</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 2: Chlorinated Fresh Water</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 3: Deoxygenated Fresh Water</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Tank 4: Chlorine Dioxide Treated Fresh Water</b>	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights	3 replicates x 3 tank heights
<b>Total Specimen per Tank</b>	54					

### 6.1.2 Freshwater Simulation

Corrosion effects due to ballast water management systems operated in a freshwater environment will be researched in Phase 2: Corrosion Rate Assessment. It is not practical to use Great Lakes supplied freshwater for these experiments, and the Naval Research Laboratory in Key West, FL is not located near a source of natural freshwater. Therefore, the freshwater environment will be simulated using municipal, potable water that is supplied by the FKAA.

The primary supply of groundwater for FKAA is the Biscayne Aquifer near the Everglades National Park in southern Florida. The Biscayne Aquifer is supplemented with the Floridan Aquifer, a brackish groundwater source. The Floridan Aquifer is the source for the FKAA reverse osmosis plant. The groundwater from the Biscayne Aquifer is classified as very hard due to the high concentration of calcium in the water. A process called lime softening is used to reduce the calcium hardness. The

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softened water is then filtered through dual media filters of sand and anthracite. After filtering, chlorine and ammonia are injected into the water to form chloramines which disinfect the water. Fluorine is also added to the water. The water is then pumped 130 miles to Key West through steel piping.

Freshwater from lakes is different from freshwater from a municipal water treatment plant. Freshwater from lakes will contain organisms, contaminants, and may have additional organic and inorganic content that will not be in potable drinking water. It is not uncommon for a lake to have chlorides, as evidenced in Lake Superior due to run-off from streets which used salt for deicing. Chloride content in several locations of Lake Superior was measured between 1 and 21 mg L<sup>-1</sup> (Ray, Lee, & Little, 2009). The water was also slightly alkaline (pH 7.5 to 8.5) and oxic (7 to 9 mg O<sub>2</sub> L<sup>-1</sup>). Many of these locations were near shipping piers, so there is some evidence that this water could end up in ballast tanks.

Measurements of FKAA tap water at NRLKW yielded a pH range of 8.5 to 9.3, a dissolved oxygen concentration of ~7.7 mg L<sup>-1</sup>, and 0.5 parts per thousand salinity. Generally speaking, a higher pH and lower oxygen content will decrease the rate of corrosion, whereas a higher salinity level will increase the rate of corrosion. NRLKW proposes to monitor water chemistry parameters for pH, dissolved oxygen, and chloride content of FKAA water during the freshwater experiments. RDC will discuss with NRLKW how to best replicate the conditions and water chemistry of the Great Lakes.

### 6.2 Phase 2: Shipboard Testing

As part of Phase 2 of the project, two vessels will be identified and recommended as test platforms for the shipboard testing. One vessel will be a freshwater “Laker” that operates in the Great Lakes and the other will be a “Salty” that operates in seawater. The objective is to determine how treatment systems affect the rate of corrosion in ballast tanks during field tests.

Several freshwater Lakers have been identified as potential platforms for ballast tank corrosion testing. These vessels are of particular interest because the ballast tanks are uncoated, making them more susceptible to corrosion.

Several saltwater vessels, which are currently enrolled in the USCG’s Shipboard Technology Evaluation Program (STEP), have also been identified as potential platforms. STEP provides ship owners and technology manufacturers incentives to develop, install, and test experimental or prototype treatment systems. STEP benefits USCG by allowing tests and research to be performed on the experimental treatment systems. STEP benefits vessel owners accepted into the program by granting them an equivalency or reprieve to meet the future ballast water discharge standards for up to the life of the vessel or the system while the system operates satisfactorily. One of the STEP vessels in Table 11 will be selected as the “salty” test platform for the shipboard phase.

Table 11. USCG STEP vessels. (Shipboard Technology Evaluation Program (STEP), 2011)

Ship, Official Number, Owner	Technology	Docket #
CORAL PRINCESS #9229659 <a href="#">Princess Cruise Lines</a>	<a href="#">Hyde Marine Systems</a>	<a href="#">2007-0040</a>
MOKU PAHU #649569 <a href="#">Matson Shipping</a>	<a href="#">Ecochlor Inc.</a>	<a href="#">2007-0041</a>
ATLANTIC COMPASS #8214176 <a href="#">Atlantic Container Lines</a>	<a href="#">Ecochlor Inc.</a>	<a href="#">2007-0042</a>
S/R AMERICAN PROGRESS # 1053997 <a href="#">Sea River Maritime, Inc.</a>	<a href="#">SevernTrentDeNora</a>	<a href="#">2008-0126</a>
APL ENGLAND #9218650 <a href="#">APL Limited</a>	<a href="#">NEI Treatment Systems</a>	<a href="#">2009-0739</a>
CELEBRITY MERCURY # 9106302 <a href="#">Celebrity Cruises</a>	<a href="#">Hyde Marine Systems</a>	<a href="#">2009-0995</a>



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