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Vessel-Generated Ballast Water; Gray Water Investigation

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16 Abstract (MAXIMUM 200 WORDS)				
This report describes a study conducted to e	xamine the feasi	hility of gray water halla	sting on cruise shins a	nd
related correction issues. Mass loss and elec	trachemical corr	osion experiments were	performed on A36 stee	
coupons with simulated gray water (treated	and untrasted)	equater and mixtures of	arow water and service	tor
coupons with simulated gray water (treated and untreated), seawater, and mixtures of gray water and seawater.				
The seawater samples had a greater corrosion rate in grams per square meter per day (gm/m ² /day) than the gray				
water samples, however, trends for the other types of gray/seawater mixtures differed between the two experimental				
methods. Corrosion rates for the electrochemical study were approximately 3-5 times greater than that for the mass				
loss study, primarily because the electrochemical tests measured <i>initial</i> corrosion rates only, and the mass loss rates				
were overall rates over 50 days.				
Cycled conditions (where the steel coupons were regularly submerged and un-submerged to simulate fluctuations in				
ballast-tank water levels) resulted in the gre	atest mass loss.	For coated/scribed coupo	ons, untreated grav wa	ter was
more corrosive than seawater for humid and	cycled condition	ns. For mixtures of grav	water and seawater. c	orrosion
trends were unclear; and for uncoated samp	les there was a sl	arp pH decline for seaw	ater in humid and cvcl	ed
conditions				•••
A sinploard reasoning analysis on a large c	uise snip, snowe	ed that gray water could t	lly as hallost may not	ast on a
typical transit from New York, NY to Bermuda; nowever, use of gray water specifically as ballast may not be				
practical given the installed systems for treating and storing gray water, waste water, and ballast water aboard the				
particular vessel.				
Discussion with two "small" cruise ship operators that transit from coastal to fresh water (including the Great				
Lakes) indicated that for their purposes, production of gray water offset potable water and fuel use for these transits,				
and since their destinations are often "no-discharge" zones, held gray water onboard until a port call.				
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EXECUTIVE SUMMARY

The Coast Guard (CG) Research and Development Center (RDC) tasked a United States Coast Guard Academy (USCGA) capstone design team to examine the feasibility of using gray water¹ as ballast aboard ships as a way to mitigate transfer of invasive species when ballasting with seawater, and issues with gray water discharge. There were two major objectives for the study. One objective was to use both" mass loss" and electrochemical methods to explore the effects of corrosion on ballast tank materials exposed to simulated cruise ship gray water (treated and untreated), standardized seawater (ASTM D1141-98), and two proportional mixtures of untreated gray water and seawater. A second objective was to perform a shipboard feasibility study for a particular cruise ship using ship plans and data provided on ballasting practices, wastewater management practices, and ship operations to examine the feasibility of gray water ballasting for that ship.

The mass loss experiment used two types of 1" x 1" A36 steel "coupons:" uncoated and epoxy coated with a ¹/₄ inch diameter uncoated "dot" or "holiday" to simulate unintentional damage to the coating in a typical ballast tank. The A36 coupons were subjected to five water types described above over a 50 day period at a temperature of 35 degrees Celsius (C). Three different exposure scenarios were used to simulate the ballast tank environment: submerged, humid, and cycled weekly between humid and submerged. The electrochemical tests were only run on coated/scribed samples under submerged conditions for the specific purpose of correlating results from lengthy mass loss tests with more expedient electrochemical methods.

The results of the mass loss study revealed greater loss of material for the cycled samples compared to humid and submerged protocols as would be expected, due to the repeated exposure of the coupons to surface water rich in dissolved oxygen. The cycling simulated conditions near the top of a ballast tank at the air/water interface or splash zone. For the coated/scribed samples less overall mass loss occurred in total grams; however, the corrosion rate when normalized to $g/m^2/day$ were actually higher compared to the uncoated samples. This difference in corrosion rate is due to the small ¹/₄ inch area of metal exposure in the holiday, which exacerbates local potential differences that drive local corrosion. Visual evidence of the metal/coating interface showed localized pitting of the metal/epoxy interface. The coated/scribed samples showed greater mass loss in seawater compared with untreated gray water for the submerged condition; however, for the humid and cycled samples the untreated gray water produced greater mass loss than did the seawater. For the uncoated samples, the seawater produced greater mass loss under all exposure scenarios. The pH of the final seawater in the mass loss beakers fell from 7.99 to between 4 and 5 for uncoated samples under the cycled and humid environments; however, for the submerged condition the pH was relatively neutral throughout the experiment. In all cases, the 5-day biological oxygen demand (BOD₅) of the gray water fell by more than 90% over the 50 day experiment indicating that aerobic biological activity was robust. This biological activity was also observed when gray water was mixed with seawater. For both coated/scribed and uncoated samples, pH of the untreated gray water increased from 5.5 to above 7.5. Reactions in the gray water over time appeared to increase pH and alkalinity over time, however, further testing would be needed to identify those interactions.

The electrochemical corrosion tests were conducted in triplicate on coated/scribed coupons that were polished and submerged in the five water solutions. A Pine Instruments 3-electrode corrosion cell was used

¹"Gray water" generally refers to all wastewater generated from sources without fecal contamination, i.e. all wastewater streams except wastewater from toilets. Sources include laundry, shower/baths, sinks, or galley cleaning equipment, among others. We assume gray water contains fewer pathogens than wastewater from toilets.



for coupon testing. Anodic and cathodic sweeps were conducted using a potentiostat to vary the overpotential \pm 180 mV from the open circuit potential (OCP). Tafel plots were generated to determine the corrosion current (i_{corr}), which were then normalized based off the known exposed holiday area and converted to mass loss rates in g/m²/day. Electrochemical testing requires the sample coupon be in constant contact with the solution, which is why only submerged coupon testing was performed by electrochemical methods.

Both mass loss and electrochemical tests showed that coated/scribed submerged coupons in seawater had a higher corrosion rate than did coupons in the untreated gray water. Although, the trend was the same, the rates of corrosion in $g/m^2/day$ were between 2.9 and 5.25 greater for the electrochemical tests compared with the mass loss testing. The electrochemical corrosion rates reflect initial corrosion of the coupons; whereas, the mass loss study results represent an overall corrosion rate over a 50 day period of submersion in the test solutions. Additional electrochemical testing, conducted at various time intervals as the coupons corrode in solution would provide a valuable indication of whether short-term electrochemical testing that identifies initial rates can be used to model long term corrosion.

Based on mass loss and electrochemical testing, results involving the mixtures of gray water and seawater were inconsistent and difficult to explain. The mixtures may trigger a more complex set of reactions compared with corrosion reactions in gray water or seawater alone.

In addition to the corrosion studies, a feasibility analysis of gray water ballasting examined ship systems and trim conditions to determine if it is possible to ballast with gray water. A typical New York-Bermuda transit of the M/V Norwegian Breakaway cruise ship served as the test case. Trim calculations based on the loading changes caused by gray water generation and fuel burn rates show that gray water can be used to supplant seawater as ballast aboard this cruise ship. However, based on the analysis and discussion with the vessel crew, this practice may be unnecessary due to modern systems onboard the ship to treat combined gray and black water to very low contaminant levels for overboard discharge, and multiple, installed ballast water treatment systems.

The results indicate that it may be feasible to ballast with gray water on large cruise ships, but the practicality depends on present and emerging regulations, current ship systems versus potential modifications, and further analysis of corrosion issues. The project did not investigate whether either wastewater or ballast water treatment systems could effectively treat a gray-water/ballast water mix. Further study should include the complexities of corrosion rates and better understanding of chemical and biological reactions mediating corrosion in ballast tanks (including identification of any important microorganisms and their effect on corrosion rates). It is also recommended to focus on gray water and seawater comparisons rather than looking at mixtures and to run electrochemical tests on coupons at various stages of corrosion over time. Possible gray water ballasting on small cruise ships and government vessels should also be explored in future studies.



TABLE OF CONTENTS

ACI	KNOWLEDGEMENTS	v
EXI	ECUTIVE SUMMARY	vii
LIS	ST OF FIGURES	xi
LIS	ST OF TABLES	xii
LIS	ST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS	xiii
1	INTRODUCTION	
1.	.1 Problem Statement	
1.	.2 Background Information	1
1.	.3 Objectives	1
2	LITERATURE REVIEW	2
2.	2.1 Corrosion Experiments	2
_,	2.1.1 Mass Loss Experiments	
	2.1.2 Electrochemical Corrosion Experiment	7
2.	2.2 Regulations Governing Gray Water and Ballast Water from Ships	11
	2.2.1 Gray Water Discharge Regulations	11
	2.2.2 Ballast Water Regulations	11
2.	2.3 Cruise Ship Gray Water Generation and Treatment	12
	2.3.1 Cruise Ship Gray Water Composition and Quantity	12
	2.3.2 Wastewater Treatment Systems Aboard Ships	
2.	Ballasting Practices and Ballast Water Treatment Methods	
	2.4.1 Ballast Water Management and Treatment	16
3	CORROSION EXPERIMENT MATERIALS AND METHODS	19
3.	8.1 Materials	19
	3.1.1 Simulated Gray Water and Seawater Recipes	19
	3.1.2 Mass Loss Experiment Materials List	20
_	3.1.3 Electrochemical Analysis Materials List	
3.	5.2 Methods	
	3.2.1 Mass Loss Experiment	
4	ALTERNATIVE METHODS	28
4.	.1 Sample Preparation Alternatives	
4.	Alternatives for Prepping Samples at the end of the Mass Loss Experiment	
4.	Cruise Ship Selection Alternatives for the Feasibility Analysis	
5	RESULTS AND DISCUSSIONS	29
5.	5.1 Mass Loss Corrosion Experiment Results	29
	5.1.1 Quantitative Results	29
	5.1.2 Qualitative Results	34
5.	5.2 Electrochemical Corrosion Results	35
5.	5.3 Comparison of Mass Loss and Electrochemical Experiments	36



TABLE OF CONTENTS (Continued)

5.4 Shipboa	rd Feasibility Analysis Results	
5.4.1 Large	Cruise Ship	
5.4.2 Small	Cruise Ships	
6 CONCLUSI	ONS AND RECOMMENDATIONS	41
6.1 Conclus	sions and Recommendations: Corrosion Studies	
6.2 Conclus	sions and Recommendations: Feasibility Study	
6.3 General	Conclusions	
7 REFERENC	ES	
APPENDIX A.	MASS LOSS DATA	A-1
APPENDIX B.	ANALYSIS OF TEST WATER	B-1
APPENDIX C.	Mass LOSS PHOTOGRAPHS (MICROSCOPE)	C-1
APPENDIX D.	MASS LOSS WHOLE SAMPLE PICTURES	D-1
APPENDIX E.	ELECTROCHEMICAL EXPERIMENT TAFEL PLOTS	E-1
APPENDIX F.	SHIP CALCULATION SPREADSHEETS	F-1
APPENDIX G.	SHIP CALCULATIONS	G-1
APPENDIX H.	SHIP TANK CAPACITY DIAGRAMS	H-1



LIST OF FIGURES

Figure 1. Example of the corrosive effects on a hull and appendages	2
Figure 2. Traditional corrosion of iron in water.	
Figure 3. Addition of rare earth oxides decrease overall weight gain of stainless steel 304L	5
Figure 4. Typical long-term corrosion experiment setup	5
Figure 5. Mass loss over time curve for corrosion of 403 Ferretic Stainless Steel	6
Figure 6. Schematic of the anode-cathode process.	
Figure 7. Galvanic series of common ship metals.	9
Figure 8. Electrochemical experiment coupon set-up	
Figure 9. Membrane bioreactor treatment system.	14
Figure 10. Example of plastic media used to attract bacteria.	15
Figure 11. Righting moment.	16
Figure 12. European zebra mussels filling a beach in the Great Lakes	
Figure 13. Open-ended ballast tubes.	
Figure 14. Original coupon construction (from left to right): A36 steel, brass, and aluminum with	
attached copper wire sealed in epoxy	
Figure 15. Pine Instruments 3-electrode 1L corrosion cell.	
Figure 16. Tafel Plot of A36 steel in simulated ocean water	
Figure 17. Comparative corrosion rates of Brass, A36 and Al 6061 in seawater	
Figure 18. Mass loss for coated/scribed samples (average of replicates).	
Figure 19. Mass loss for uncoated samples (average of replicates).	
Figure 20. Relative loss in metal thickness based on depth in water	
Figure 21. BOD ₅ decline over time for gray water in the mass loss incubator	
Figure 22. Electrochemical corrosion rate for coated/scribed coupons by water type	
Figure E-1. Electrocorrosion Tafel plot, 25% gray water/75% seawater.	E-1
Figure E-2. Electrocorrosion Tafel plot, 75% gray water/25% seawater.	Е-2
Figure E-3. Electrocorrosion Tafel plot; 100% gray water	Е-2
Figure E-4. Electrocorrosion Tafel plot; 10% gray water/90% distilled water.	Е-З
Figure E-5. Electrocorrosion Tafel plot; 100% seawater	Е-З
Figure G-1a. Handwritten vessel operations, consumption, and production calculations	G-1
Figure G-1b. Handwritten vessel operations, consumption, and production calculations	G-2
Figure G-1c. Handwritten vessel operations, consumption, and production calculations	G-3
Figure G-1d. Handwritten vessel operations, consumption, and production calculations	G-4
Figure G-1e. Handwritten vessel operations, consumption, and production calculations	G-5
Figure G-1f. Handwritten vessel operations, consumption, and production calculations.	G-6
Figure G-1g. Handwritten vessel operations, consumption, and production calculations	G-7
Figure G-1h. Handwritten vessel operations, consumption, and production calculations	G-8
Figure G-1i. Handwritten vessel operations, consumption, and production calculations.	G-9
Figure G-1j. Handwritten vessel operations, consumption, and production calculations.	G-10
Figure H-1. Treated waste water tanks.	H-1
Figure H-2. Potable water tanks	H-2
Figure H-3. Fuel tanks.	H - 3
Figure H-4. Ballast tanks.	H-4



LIST OF TABLES

Table 1. Simulated gray water recipe.	19
Table 2. Simulated seawater recipe.	20
Table 3. Mass-loss materials list.	20
Table 4. Results from initial electrochemical testing using different metals	
Table 5. Initial and final composition of mass loss test water for coated/scribed samples	32
Table 6. Initial and final composition of mass loss test water for uncoated samples.	
Table 7. Electrochemical corrosion rates by water type	35
Table 8. Mass loss and electrochemical results for submerged coated/scribed samples	
Table 9. Loading conditions for various scenarios on the Norwegian Breakaway.	
Table 10. Final forward and aft drafts estimated for the Norwegian Breakaway	
Table A-1. Mass Loss Data for individual test coupons.	A-1
Table A-2. Average Mass Loss Data.	A-3
Table A-3. Average mass-loss rate.	A-4
Table B-1. Analysis of test water at beginning of of mass loss (17 Feb) and electrochemical	
experiments (all other dates)	B-1
Table C-1. Photographs of coated/scribed sample coupons.	C-1
Table C-2. Photographs of uncoated sample coupons.	C-4
Table D-1. Photographs of coated/scribed sample coupons.	D-1
Table D-2. Photographs of uncoated sample coupons	D-3
Table E-1. Electrochemical mass-loss results	E-1
Table F-1. Vessel Trim Calculations – mid-ocean.	F-1
Table F-2. Vessel Trim Calculations – leaving Bermuda	F-2



LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

А	Surface area (in^2)
ACSI	Alaska Cruise Ship Initiative
AOT	Advanced oxidation technology
BOD ₅	5-day Biochemical Oxygen Demand
С	Celsius
COD	Chemical Oxygen Demand
cm ²	Cubic centimeters
CWA	Clean Water Act
D	Density (g/m^3)
Е	Overpotential (volts)
EPA	United States Environmental Protection Agency
g/m ² /day	Grams per square meter per day
GW	Gray Water
i	Current density (mA/cm^2)
i _{corr}	Corrosion current
IMO	International Maritime Organization
LBP	Length between perpendiculars
LCF	Longitudinal center of flotation
MBR	Membrane bioreactor
MBBR	Moving bed biofilm reactor system
m ³ /h	Cubic meters per hour
mA	Milliamps
mL	Millilters
mm	Millimeters
MPY	Mils penetration per year
NACE	National Association of Corrosion Engineers
NPDES	National Pollutant Discharge Elimination System
OCP	Open circuit potential
SW	Seawater
Т	Time of Exposure
TKN	Total Kjeldahl Nitrogen
ТР	Total phosphorous as P
TSS	Total Suspended Solids
USCGA	U.S. Coast Guard Academy
UV	Ultraviolet
W	Mass loss in mg



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1 INTRODUCTION

1.1 Problem Statement

Environmentally sound methods for seawater ballasting and gray water discharge are needed that comply with applicable regulations while minimizing operational and corrosion issues.

1.2 Background Information

Ballast water management is a continuing area of concern aboard ships. While necessary for stability, ballasting with ocean water has become a mode of transportation for invasive marine organisms from one port to another. Another area for concern is gray water production, treatment, and disposal. Gray water is water from sinks, showers, drains, and galleys onboard a ship. While some ships practice water-saving techniques to mitigate gray water generation, others such as cruise ships generate enormous amounts of gray water containing a variety of pollutants that are potentially harmful to the marine environment. Existing and future regulations governing discharge of gray water from ships will increase the urgency of developing alternative gray water management techniques in the years to come. A key issue with gray water is its potential for tank corrosion.

In the spring of 2014, a capstone design team at the U.S. Coast Guard Academy (USCGA), sponsored by the Coast Guard Research and Development Center, studied the feasibility of ballasting with gray water on cruise ships to evaluate whether challenges with management of ballast water and gray water can be addressed together. Simulated cruise ship gray water was effectively treated in a lab-scale membrane bioreactor (MBR) and a preliminary feasibility analysis of ballasting with gray water on cruise ships was conducted. This previous work led to follow-up independent study and capstone effort during the 2014-2015 academic year.

1.3 Objectives

The 2014-2015 project had the following objectives:

- Conduct a long-term mass loss study to examine potential corrosion of typical ballast tank material (A36 steel coated and scribed and uncoated A36 steel) exposed to cruise ship gray water (treated and untreated), seawater, and mixtures of gray water and seawater in submerged, cycled, and humid environments.
- Compare results of the long-term mass loss corrosion experiment with results of short-term electrochemical corrosion experiment using the same coupon materials and water types.
- Evaluate the feasibility of gray water ballasting for a typical ocean-going cruise ship and/or a smaller-sized cruise ship operating in the Great Lakes in the context of legal, operational, ship stability, and environmental considerations. Assessment should include an examination of ballasting rates and practices, gray water generation rates, and existing ballast and wastewater storage and treatment systems.



2 LITERATURE REVIEW

2.1 Corrosion Experiments

2.1.1 Mass Loss Experiments

Corrosion is an area of increasing interest among the engineering community. In the corrosion process building materials such as steel, aluminum, copper, and cast iron give up ions resulting in a reduction of mass and strength of the material. Corrosion provides a visible measure of the age and structural deficiency of a structure, ship or other object. Corrosion is responsible for the degradation of shore structures and shorter service lives for ships and aircraft. Generally, the term corrosion only applies to metals or metallic alloys. Corrosion can be a detriment to society if left unchecked. Corrosion has caused plane crashes, automobile accidents, bridge collapses, and many other engineering disasters. One such bridge collapse in Pt. Pleasant, West Virginia, killed over 40 people. The cause of failure was determined to be stress corrosion cracking (Jones, 1992).

Universities, industry, and various research organizations have devoted much time and money to studying the causes, rates, and effects of corrosion and are actively exploring corrosion prevention techniques. For decades, long-term mass loss experiments have been used to determine corrosion rates of materials. The process typically involves exposing a small sample of metal in a given environment over a long period of time. The sample is weighed periodically over a given span of time and the mass loss over time is converted to a corrosion rate for the sample in mils of penetration per year (MPY).

The Coast Guard has a vested interest in understanding and reducing the effects of corrosion on their ships. By reducing corrosion, the Coast Guard and other maritime services can prolong the service life of their assets and save the government from incurring huge corrosion related expenses and risk. Figure 1 shows hull and appendage corrosion.



Source: (http://www.offshore-mag.com/articles/print/volume-71/issue-12/production-operations/remedial-design-restores-cathodic-protection-tocorrosion-damaged-hull.html)

Figure 1. Example of the corrosive effects on a hull and appendages.



Vessel Generated Ballast Water; Gray Water Investigation

The exposed metal may give electrons and corrode, or it may be protected by less noble metals. A protective coating is created through a series of cathodic and anodic reactions that cause a metal to either give or receive charged ions (corrosion-doctors.org 2014). By giving ions to the surroundings, the metal begins to lose some of its mass. By measuring the mass loss, a corrosion rate can be calculated as a function of time. This is the basis of long-term corrosion experiments.

While the rates and extent of corrosion varies from material to material, the typical reaction for corrosion remains similar; that is, a metal oxidizes giving its electrons to reduce oxygen in the presence of water. The basic equation for the oxidation of steel in water is shown in Equation (1), while Equation (2) shows the formation of rust after the initial oxidation.

(1) $4Fe + 6H_2O + 3O_2 \rightarrow 4Fe(OH)_3$ Oxidation of iron in water

(2) $2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$ Rust formation after initial oxidation of iron

These two equations represent the basis for the mass-loss, long-term corrosion experiments (corrosion-doctors.org, 2014). If ferrous metal (steel) is allowed continuous exposure to atmosphere, then the steel will continue to lose mass and strength until eventually it will fail under stress.

The oxidation and rusting of steel is a result of anodic and cathodic reactions, in which electrons are supplied and taken to form ions, which react with other ions to form the iron oxide. The reaction is shown below in Figure 2.



Source: (Wright, 2015)





The anodic site loses an iron ion and two electrons, while oxygen is supplied from the surrounding environment and accepts the two electrons from iron at the cathodic site. These new ions form the iron oxide.

Zinc is a common metal that is often used as a sacrificial anode in marine environments because it more easily gives up its electrons instead of the steel it is attached to. The oxidation and loss of material in the formation of the zinc oxide protective layer follows a trend similar to iron and other metallic alloys (Jones, 1992).

Traditional corrosion experiments involve placing a metal sample in a corrosive environment and massing the sample at regular intervals over a long period of time. One of the benefits of a mass loss experiment is that the variables can be altered fairly easily.

The material of the sample is one of the main variables to be explored. Most metals and metal alloys corrode. Due to extensive use of steel and iron in ships, reinforced concrete beams, structural steel beams and girders, fences, sheet piles, and a host of other applications these metals have been studied for corrosion effects. Aluminum is another common sample type. Aluminum is used in aircraft parts and other applications where lightweight materials are needed. Brass, copper, and other materials are also used in construction applications and are of interest in corrosion studies (Jones, 1992). One application where the corrosion rate is extremely useful is zinc sacrificial anodes. The zinc will be electronically connected to a corrosion-prone material and thus serve as a sacrificial donor of ions to preserve the construction material. By knowing the corrosion rate of the sacrificial anode, the engineer, designer, or customer can then know how long the main structure is protected with a certain size anode (Vera et al., 2013).

Another test variable that can be altered is the environment in which the sample rests. The environment that the sample is exposed to can be tailored to the specific operational environment in which the actual metal structure is going to be placed. In addition to laboratory testing, the experiment can be carried out in-situ. In-situ testing will yield a better indication of what the actual specimen or structure may experience; however, variables are more difficult to control (Vera et al., 2013).

Another major variable that affects corrosion is exposure time. The time an object is left to corrode can greatly affect the overall mass loss. Time periods used in mass loss experiments typically range anywhere from 182 days to 5 years (NACE, 2012) (Gdowski, 1997). Generally, the longer an object is exposed the more mass is lost through corrosion. The frequency of measurement; however, can affect the mass loss. If the rust coating is left on the sample, the measurement can also be affected. The coating can protect the sample from further corrosion. Figure 3 is a weight gain versus time curve that shows how rare earth oxides decrease the overall weight gain compared to stainless steel 304L without any additives. (Pillis, et al., 2006).The more that thickness increases due to oxidation, the more mass is lost by the specimen, in general. Upon examination, the scaling will be scraped away from the specimen before it is massed (Paik et a.l, 2004).





Source: (Pillis et al., 2006)

Figure 3. Addition of rare earth oxides decrease overall weight gain of stainless steel 304L.

The mass loss experimental setup can vary greatly from experiment to experiment. Figure 4 shows one common type of lab setup for mass loss testing. A cylindrical glass jar, opaque plastic container, or corrosion resistant material is used to contain the experiment so that the cell itself does not affect the experiment (Lee et al., 2004). The glass is non-reactive, so it will not influence the extent of the corrosion in the sample. The sample is then suspended in the glass jar by a variety of means. A stand may be submerged in the water along with the sample or the sample may be hung from a stand. Care must be taken to ensure that the area around the connection to the stand is coated or electronically grounded so that the sample does not corrode as a result of the connection rather than the sample's natural corrosion rate in a given environment.



Source: (Williams, 1996) Figure 4. Typical long-term corrosion experiment setup.



Vessel Generated Ballast Water; Gray Water Investigation

In many cases, the surface of the sample is prepared in specific ways. The sample is either heat treated, sandblasted to a specific surface profile, or coated with different materials, depending on the experiment being performed (NACE, 2012). The samples are left to sit in the cell for a specified amount of time. The samples will be massed at the beginning and periodically throughout the experiment (Williams, 1996).

Data collection can include many different parameters for any given corrosion experiment. The different types of corrosion to be explored are "general corrosion, pitting corrosion, crevice corrosion, stress-corrosion cracking, and galvanic corrosion" (Gdowski, 1997). The sample is massed at a given time and the data are recorded. Figure 5 is a log-log plot that represents a typical mass loss over time for a long term experiment for different steel alloys.



Source: (Alonso-Falleiros & Wolynec, 1998)



The corrosion rate can then be calculated in MPY.

$$(3) MPY = \frac{534 W}{DAT}$$

where W is the mass loss in mg; D is the density, g/cm^3 ; A is the exposed surface area, in^2 of the sample that is exposed to the elements, and T is the time of exposure in hours, h. This corrosion rate is used to compare samples, estimate service life, and has other uses as well (Jones, 1992).

In addition to the mass loss data, visual observations are also an important component of a corrosion experiment. Visual observations of the sample can show the amount and pattern of corrosion. The experimenter typically will be able to tell if the sample is sufficiently corroded to obtain a solid mass loss data point. Accepted techniques for visual identification of a sample often include the aid of microscopes.



Vessel Generated Ballast Water; Gray Water Investigation

Two such microscopes used in mass loss experiments are light optical microscopy and scanning electron microscopy (Paik, et al., 2004). The National Association of Corrosion Engineers (NACE) lists a very specific and detailed experiment for determining the effects of corrosion on ballast water systems. The set up and initial preparation of the sample includes using a small, low alloy steel blank. The blank should measure 400mm by 200mm by 3mm, be coated with an appropriate marine ballast tank coating, and then the coating is scribed to simulate damage to the tank. Multiple samples are prepared to ensure consistent results. The samples are placed at a temperature of 35°C. This simulates the environment the actual steel in a ballast tank will experience. The specimens will be either left submerged, exposed to humid air, or cycled between submerged and humid conditions to simulate the movement of the water in the ballast tank. The specimens are to be exposed to the environment for as close to the NACE standard of 182 days as practicable.

Two methods of examining the effects of corrosion can be used, a visual examination using a microscope and a mass loss calculation. The specimens are examined under a microscope for the onset of corrosion as well as any other defects in and around the area of the scribe. The specimens are massed after the conclusion of the test to determine a rate of corrosion (NACE, 2012). By knowing and understanding the visual indicators of corrosion, an inspector or designer can see when an object is nearing the end of its service life or is in need of a renovation.

The study of corrosion is extremely important with long standing implications for future engineering designs as well as the renovations of existing structures. Long-term experiments offer both visual and mathematical results, which can then be used to determine the corrosion rate. From the corrosion rate of a given material in a given set of environmental conditions, a useful service life can be estimated and ways to mitigate or prevent corrosion can be explored. The process can be used to recreate specific conditions and be adapted for almost any application.

2.1.2 Electrochemical Corrosion Experiment

Long-term mass loss experiments have a major drawback in that it takes months, if not years, to determine corrosion rates. By using shorter-term experiments to determine corrosion rates and correlating these results with those of longer term studies, it may be possible to gather corrosion data under a variety of conditions in much less time compared with conventional mass loss studies.

Through the use of a corrosion cell, the process of metal corrosion can be accelerated by the use of electrochemical techniques. Galvanic corrosion takes place when two different metals come into contact with a conductive liquid -- usually impure water or soil moisture -- resulting in a flow of direct current electricity (SESCO, Inc., 2015). Ships are particularly vulnerable to this type of corrosion for they are constantly in contact with either salt water or fresh water. In nature, this process happens naturally; however, connecting a potentiostat to the corrosion cell allows a controlled stream of electrons to be either pushed in or pulled out of the metal sample inducing experimentally controlled and easily monitored electrochemical driving force between opposing electrochemical half-reactions. The first is the anodic reaction, in which a metal is oxidized; thereby releasing electrons from the metal that travel towards the cathode through a conducting wire. The other is the cathodic reaction, in which a solution species (often dissolved O₂ or H⁺(aq)) is reduced at the cathode surface by removing electrons from the metal (Gamry, 2015). The anode is corroded as electrons flow away from the anodic metal. The electrical circuit is completed as charge flows in the form of ions through the electrolyte solution. Anions carry (–) charge to



the anode, while cations carry (+) charge to the cathodic metal (cathode). In this process the cathode is not corroded; however, the anode slowly degrades (gordonengland.co.uk, 2015). Figure 6 shows a schematic of the electrochemical process.



Source: (Paik, et al., 2004)

Figure 6. Schematic of the anode-cathode process.

The method to determine the corrosion rate uses a potentiostat to apply an overpotential to the metal coupon. The measured current (i) is directly related to the overpotential by the Tafel equation (Bard and Faulkner, 2001):

$$(4) E = a + b(\log i)$$

where E is the overpotential measured in volts; 'a' and 'b' are constants; and 'i' is the current density measured in mA/cm². The 'b' constant is known as the Tafel slope. Both anodic and cathodic sweeps exhibit a constant Tafel slope unique to the surface electrochemistry as the overpotential increases beyond about ± 50 mV. The linear Tafel regions each have a linear trendline that intersects at the systems open circuit potential (OCP) where the overpotential is zero. This intersection of trendlines provides the corrosion rate of the metal (i.e. i_{corr}) which can then be converted to a mass loss rate in mils per year using Faraday's Law.

Through measuring the anodic and cathodic capabilities of the metals and comparing them to published values, a corrosion reactivity series can be developed. This experimentally determined reactivity series could also be compared to published sources on submerged marine metals. This series can then be used to show the varying nobilities of metals and one can rank their usefulness for construction in various ship structures. Depending on the environment that each unique ship structure is subject to, corrosion resistant materials can be selected. This has far-reaching implications when it comes to structural integrity, maintenance, and lifespan of vessels. By identifying the best metals dependent on each marine environment found onboard a ship (submerged, cyclical inundation, air exposure), one could potentially optimize ship design and operation to be highly resistant to corrosion and its destructive and costly effects.



The tendency to corrode depends on where a metal falls in the galvanic series as well as what type of solutions/materials the metal is in contact with, environmental conditions, and a number of other factors. The galvanic series for various types of metal are shown in Figure 7.



Source: (kastenmarine.com, 2015)

Figure 7. Galvanic series of common ship metals.

As a metal oxidizes, a protective layer may form which blocks the metal's contact to the surrounding water and retards the corrosion process. In the case of aluminum, a durable aluminum oxide patina is formed and is far harder and more resistant to physical breakdown and chemical attack than its iron oxide counterpart. An aluminum-oxide patina is formed immediately in the presence of oxygen. This is why the Al-6061 shows a great reduction in its corrosion rate once the patina layer forms making it less reactive than A36



Vessel Generated Ballast Water; Gray Water Investigation

steel in the reactive series when exposed to air & seawater. If aluminum did not form an oxide layer then it would easily give up its electrons to more noble metals and would perform as suggested in the galvanic series shown in Figure 7.

Brass undergoes a different process known as "dezincification" when submerged in seawater. Dezincification is an example of "dealloying" in which one of the constituents of an alloy is preferentially removed by corrosion. Brass is a metal alloy composed or both copper and zinc. While the copper is quite unreactive in the galvanic series, the zinc is prone to quick corrosion. In studies rising from copper condensing tubes in the 1920s, it was discovered that service in seawater or brackish water produced dezincification in susceptible brasses. For this reason, the zinc that is present in brass alloys undergoes a rapid corrosion cycle that prevents any formation of a protective layer and thus corrodes at a high rate (The Hendrix Group, 2015).

Two aspects requiring particular care in electrochemical corrosion experiments is production of metal coupons with a precisely known exposed metal area and careful attachment of the conducting copper wire that suspends the coupon into the test solution. Coupon production, coating method, and scribing methods must be conducted carefully and with repeatability more so than with a mass loss experiment. Precise preparation of coupons is critical to being able to standardize electrochemical testing results, because the results are dependent upon knowing the exact area of exposed metal in a coupon. One method of attaching the wire to the coupon is to wrap the wire around the top of the coupon and coat the wire with an epoxy coating. Another method is to punch a hole in the top of the coupon and then insert and wrap the wire through the hole as shown in Figure 8.



Figure 8. Electrochemical experiment coupon set-up.

Notice in Figure 8 that the copper wire is coated in a protective epoxy coating. The epoxy should be easy to apply and the dried coating must be flexible and waterproof. The chemical components found in "Shoe Goo" meet the requirements for sealing the copper wire from the water environment, is easy to apply and flexible.



2.2 Regulations Governing Gray Water and Ballast Water from Ships

2.2.1 Gray Water Discharge Regulations

In 1972, Congress enacted the Clean Water Act (CWA) in an effort to keep the waterways clean and healthy. The act controls what can be discharged into the waters in the United States (EPA, 2008). Since passage of the CWA, other Acts and regulations in the United States have been passed to prevent certain sewage and gray water releases. These policies depend on location.

Section 312 of the Clean Water Act sets out the principal framework for domestically regulating sewage discharges from vessels, and is implemented jointly by the U.S. Environmental Protection Agency and the U.S. Coast Guard. "Sewage" is defined under the Clean Water Act as "human body wastes and the waste from toilets and other receptacles intended to receive or retain body wastes", and includes gray water discharges from commercial vessels (as defined at 33 U.S.C. 1322(a)(10)) operating on the Great Lakes. Under section 312 of the Clean Water Act, vessel sewage is generally controlled by regulating the equipment that treats or holds the sewage (marine sanitation devices), and through the establishment of areas in which the discharge of sewage from vessels is not allowed (no discharge zones) (EPA, 2012). However, in most other locations, gray water discharge is not included under the Clean Water Act. (EPA, 2008).

On December 21, 2000, Congress enacted an omnibus appropriation bill that included new statutory requirements for certain cruise ships discharging gray water and sewage in Alaska (33 U.S.C.1901 Note). These statutory requirements referred to as "Title XIV" requires that any large cruise ship, those approved to carry 500 or more people, and discharging within one nautical mile of shore, meet the requirements for fecal coliform and chlorine. There must not be more than 20 fecal coliform for every 100 ml sample size and less than 10 micrograms for every liter of chorine residual. This standard also applies to those ships operating at less than six-knots in any Alaskan state waters (EPA, 2008). Title XIV also requires the Coast Guard to help enforce the standards provided. Unannounced inspections of vessels, as well as requiring vessels to have logbooks of any sewage and gray water discharges, ensure vessels are in compliance. Title XIV also covers enforcement of regulations in several ways including civil and criminal penalties, and administrative orders (EPA, 2008). Lastly, the state of Alaska can request permission from the EPA to create "no discharge zones" for both gray water and sewage if deemed necessary (EPA, 2008).

2.2.2 Ballast Water Regulations

Resolution A. 774 (18), adopted by the International Maritime Organization (IMO), provides guidelines for preventing the unwanted spread of aquatic species from ballast water discharges (IMO, 1993). It states that all vessels must make every effort to only ballast clean water, avoiding shallow water. These regulations state that discharge must not exceed 10 viable organisms per cubic meter of discharge. According to this same regulation, vessels must implement a ballast water and sediments management plan. Vessels must also maintain a ballast water record book to record the amount and locations of ballast water pick up and discharge. These measures are to ensure that all vessels remain compliant with the regulations and in accordance with Resolution 774. The IMO also allows member states, which include the United States, to enforce any discharge procedures that might protect their citizens interests. The US has taken many precautions, especially in regard to water discharge in the Great Lakes. The states bordering the Great Lakes have set several standards that exceed those of the IMO or the Federal Government, including requiring special permits, and requiring all vessels entering from outside the Exclusive Economic Zone to



dispose of wastewater ashore and not into the lakes. (Minnesota Pollution Control Agency, 2014). Other nationwide regulations include the CWA. The CWA requires any "point source," which includes vessels that discharge any pollutants to have a permit. As of 2013 these discharges also include ballast water discharged from all vessels 79 feet in length and greater.

In 2012, The Coast Guard published a final rule for ballast water discharge standards. Ships will be required to either discharge ballast water to a shore reception facility, install a Coast guard approved ballast water management system, or use public water supply. As a result of the new regulations, a number of ballast water treatment systems are being tested against discharge standards set for invasive species and indicator organisms (USCG, 2012).

2.3 Cruise Ship Gray Water Generation and Treatment

2.3.1 Cruise Ship Gray Water Composition and Quantity

Cruise ships generate vast quantities of gray water, much more than any other type of vessel. The necessities, as well as the luxuries aboard, including multiple pools, restaurants, bathrooms and bars, all contribute to the quantity of gray water created. This wastewater coming from many different sources contains many contaminants including5-day biochemical oxygen demand (BOD₅), nutrients, bacteria, metal and toxic constituents. Discharge of untreated gray water could have deleterious effects on the environment and on aquatic species.

As larger cruise ships are built holding more passengers, the rates of gray water generation increase as well. Most cruise ships have storage capacity for gray water for only two to five days (ADEC, 2012). Gray water sources include the wastes from showers, laundry rooms, galleys, and sinks (EPA, 2008). Wastewater from sinks, including the galley, includes everything from food particles, bacteria, soaps, to oil and grease.

In 2004, the EPA and the Alaska Cruise Ship Initiative (ACSI), collected and tested samples from cruise ships for many constituents including fecal coliform, BOD_5 , metals, total residual chlorine, ammonia, oil and grease, and suspended and dissolved solids (EPA, 2008). The agency then compared the amount of pollutants and other components in untreated cruise ship gray water to untreated domestic wastewater which contains gray water and black water from toilets. For many contaminants, the cruise ship gray water was far more concentrated than typical domestic wastewater. For example, the average BOD_5 of cruise ship gray water was measured at 354 mg/L as compared with typical BOD_5 in weak untreated domestic wastewater which is approximately 110 mg/l (EPA, 2008). Total Suspended Solids (TSS) for cruise ship gray water averaged 704 mg/L as compared to 100 to 304 mg/L reported for untreated domestic wastewater (EPA, 2008).

Also important to include in the constituents of untreated gray water, is the amount of fecal coliform present. According to the EPA, the concentrations of fecal coliform in cruise ship gray water are one to three orders of magnitude greater than that reported for untreated domestic wastewater (EPA, 2008). ADEC data shows that the concentration of fecal coliform in cruise ship gray water is similar to the concentration in blackwater from toilets (ADEC, 2012).



In addition, the 2008 cruise ship discharge report (EPA, 2008), as well as samples taken by the ACSI, showed elevated concentrations of copper, nickel and zinc in cruise ship gray water. It is important to note that those metals are usually the materials making up the piping in ships (EPA, 2008).

The amount of gray water produced on a cruise ship depends on numerous factors. According to the Ocean Conservancy, 90,000 to 250,000 gallons of gray water per day is generated on cruise ships (Ocean Conservancy, 2004). The EPA found in its 2004 cruise ship survey, that the rate varied from 36,000 to 249,000 gallons per day. This corresponds to 36 to 119 gallons per day per person. It is estimated that 31% comes from galleys, 17% from laundry services, and 52% from various accommodations (showers, baths, sinks, etc.).

The effects of gray water are many due to its constituents. The ADEC's Science Advisory Panel expressed particular concern for localized areas where discharge comes from numerous ships that repeat the same transit routes (ADEC, 2012). BOD₅, ammonia, TSS, metals, as well as oil and grease all have an impact on surrounding ecosystems (Davis and Cornwell, 2012).

 BOD_5 can deplete the oxygen that marine life need to survive. Ammonia, also present in gray water effluent, can affect the species of phytoplankton. Certain invasive species of plankton can thrive in areas of high ammonia and takeover native species. These exotic species can be toxic to other organisms (ADEC, 2012).

The concentration of TSS harms marine surroundings in several different ways. When these solids settle in the water column, the turbidity of the water increases and oxygen available to organisms decreases (EPA, 2008). Secondly, when the suspended particles settle, habitats of certain organisms can be destroyed. This includes salmon habitats where the eggs are developing in streambeds. When the solids settle on these beds, oxygen is cutoff suffocating the eggs and reducing the salmon population (Davis and Cornwell, 2012).

Metals, including copper, nickel and zinc, endanger aquatic species as well as humans. Metals can build up in the food chain. At toxic levels, metals can modify behavioral, biochemical, and physiological patterns of marine animals (EPA, 2008). For both vertebrates and invertebrates, the accumulation of metals impacts the ability to survive and reproduce (ADEC, 2012).

2.3.2 Wastewater Treatment Systems Aboard Ships

Wastewater treatment systems on ships help ensure that wastewater will not harm the environment or aquatic life and ensure safe disposal of solids from the treatment process. In a typical land based wastewater plant, the wastewater goes through prescreening before reaching the primary clarifiers, which settle out larger solids and skim out oil and grease. Then primary effluent continues on to biological treatment to remove BOD₅ before going through final settling to remove TSS. In the activated sludge process (the most common biological treatment system), a portion of the settled solids are returned to achieve an optimum sludge age depending on treatment goals (Sustarsic, 2009). Some solids have to be removed from the process as well, as a build up of too many solids can cause a loss of solids over the effluent weir out of the secondary clarifier. After the effluent leaves the secondary clarifier, it reaches the disinfection stage. While primary and secondary treatment removes much of the solids and organics in the wastewater, disinfection is still necessary in order to remove fecal coliform. Understanding the typical wastewater treatment process is important because the shipboard systems are very similar in nature, but scaled down to size, more space efficient, and often avoiding gravity settling.



Vessel Generated Ballast Water; Gray Water Investigation

There are many systems available for treating gray water, black water, and combined gray and black water aboard various vessels. Membrane bioreactors (MBRs) are a good option for use aboard ships for many reasons. They can be designed for and operate in smaller spaces, as the filtration system of the membrane can replace the secondary clarifier and sand filters in what would be a typical activated sludge system. Because the MBRs operate at high volumetric loading rates, the hydraulic retention times are shorter, therefore resulting in less needed space.

The main difference between a typical activated sludge system and MBR systems is the membrane filtration process. By separating solids with a membrane, the need for gravity settling, which is difficult aboard a ship, is avoided. The water passing through the membrane (permeate) may not need further disinfection depending on permits and requirements (EPA, 2007). Figure 9 shows a schematic for a MBR system.



Source: (Lenntech, 2014)

Figure 9. Membrane bioreactor treatment system.

Another treatment system currently in place on cruise ships is the Moving Bed Biofilm Reactor System (MBBR). This system is versatile, and can be used as a pre-treatment system, stand alone treatment system for BOD₅ removal, nitrification, or de-nitrification, or be retrofitted to an existing activated sludge process (Brinkley et al., 2007). In a cruise ship application, the MBBR would be used as a stand alone treatment system to meet acceptable effluent levels for BOD₅, total nitrogen, and phosphorus. In an MBBR, small polyethylene media are placed in the aeration tank in order for bacteria to attach to them, which leads to a larger biomass concentration and greater biomass resiliency in the tank than that of a regular suspended growth process. The media are kept suspended by a type of mixer or aeration system, which is designed to prevent clogging and to keep the media from gathering at the bottom of the tank. Typical plastic media used are shown in Figure 10.





Source: (http://m.nkchem.en.alibaba.com/productgrouplist-))219965433/Plastic_Random_Packing.html)

Figure 10. Example of plastic media used to attract bacteria.

Another type of treatment system for both black and gray water is a physicochemical process. The physicochemical treatment process is much different than an MBR or MBBR in that it does not rely on an activated sludge process (Evac, 2014). It instead uses two separate process methods, physical and chemical. Maceration, sedimentation, and filtration are all processes found in the physical method, while the chemical method consists of coagulation, oxidation, and disinfection.

As an example, in the ORCA III sewage treatment plant, the gray and black water is transferred by macerator pump to a sedimentation tank. The gray and black water is transferred to the sedimentation tank through a static mixer and flocculation dosing. In a separate tank, the physical process ends and the chemical process begins, as the clarified liquid is re-filtered. The organic matter remaining is subject to oxidation with hypochlorite, after which the water is discharged overboard (Maritimesun.com, 2014).

2.4 Ballasting Practices and Ballast Water Treatment Methods

Ballast tanks are used by sea going vessels to increase stability. As vessels offload cargo or consume onboard stores, such as fuel and food, the displacement of the vessel decreases along with the submerged hull area. As the displacement of the vessel decreases it will tend to ride higher in the water, making it less stable overall. In most cases this decrease in onboard weight is removed relatively low in the ship, thus causing the center of gravity to rise. This can cause significant concern in elevated sea states especially when coupled with a decrease in buoyant force caused by the decrease in submerged hull area. In order to regain stability a ship must lower its center of gravity. Seawater is typically pumped into ballast tanks to bring the vessel's center of gravity down and increase the buoyant force. The distance between the center of gravity and the center of buoyancy creates a couple moment that allows the vessel to return to its upright position if the vessel heels over due to external forces acting on the ship. Since the vessel is floating, the overall weight of the ship is always equal to the buoyant force. The magnitude of the forces and their distance from each other while the ship heels, are primary indicators of the vessel's stability and is called the vessels righting moment. These parameters are demonstrated in Figure 11.





Source: (Ships & Maritime Systems Course Reader, USCGA)

Figure 11. Righting moment.

When a vessel returns to port to re-provisions and/or onload cargo, the seawater needs to be discharged so that the vessel does not become so heavy that it exceeds the hull's ability to provide an equal and opposing buoyant force. In cruise ships this entails refilling their fuel and re-provisioning their food stores. The process of taking on ballast water at one location and discharging it in another geographic region allows for the transport of aquatic species and microbes along with the ballast water. This practice brings invasive species and foreign water content to delicate shore side maritime ecosystems. Using gray water, which is normally discharged overboard, as ballast may prevent transporting seawater worldwide.

2.4.1 Ballast Water Management and Treatment

There are current cases worldwide of invasive species being transported internationally and causing huge damage to ecosystems as well as tremendous economic impact. According to the New York State Department of Environmental Conservation, approximately 65% of the invasive species introduced to the Great Lakes, including the European Zebra Mussel, have arrived via ballast water discharge. Other well known invasive species include the North Pacific seastar, the comb jellyfish, and South East Asian dinoflagellates, a microscopic algae (IMO, 2014). The magnitude of the zebra mussel problem in the Great Lakes is illustrated in Figure 12.



Source: (jrn.com, 2015) Figure 12. European zebra mussels filling a beach in the Great Lakes



Vessel Generated Ballast Water; Gray Water Investigation

The most commonly used method of alleviating invasive species spread is ballast water exchange. Current USCG regulations state that ballast water must be exchanged at least 200 nautical miles from the nearest land and in water of at least 2,000 meters in depth. If this is not possible, the minimum distance from land is decreased to 50 nautical miles while maintaining the 2,000 meter water depth (CFR Title 33 Part 151). This method can be effective because possible invasive species or organisms that live near ports are unlikely to survive in an open ocean environment with these parameters. Little time is lost with this method, as most ships exchange ballast water en route to their destination (Chase et al., undated). A major disadvantage is that not all of the organisms and species are removed from the tanks due to structural elements of the tanks that allow the organisms to stick to points within the tank. Residual species pose threats to ports, as the organisms and invasive species may then be discharged while in port.

To prevent transfer of invasive species and comply with current and impending regulations, many ships are installing ballast water treatment systems. One method used to treat ballast water is filtration. One of these systems currently in use in the industry is the CleanBallast[®] by RWO Marine Water Technology. The CleanBallast[®] system uses a two-step process including filtration followed by electrochemical disinfection (RWO, 2015). The system was designed to integrate its process both in ballast and de-ballast operations. During the filtration process, the system removes sediment and organisms while taking in ballast water. The grooves in the filter discs retain the particles and organisms. This is followed by electrochemical disinfection, which eliminates the smaller organisms and bacteria by passing an electric current through the water with electrodes (Kraft, 2008). The advantages to this filtration system are a minimal footprint and relatively low use of power (RWO, 2015). Disadvantages include the cost of installation, especially if the system is being retrofitted to the ship.

Ultraviolet disinfection is another treatment system for ballast water. The basis for using ultraviolet (UV) radiation is that is destroys the ability of a cell to reproduce (EPA 1999). The PureBallast 3.0 system by Alfa Laval AB is an example of a UV system currently in place aboard ships. At first, the water is passed through filters, which takes care of particles larger than 50 micrometers. After that takes place, the UV reactors treat the water before it enters the ballast tanks. The PureBallast 3.0 uses advanced oxidation technology (AOT) to create free radicals that cause permanent damage to the cell membrane of the organisms. Both of these processes happen while ballasting, and the de-ballasting process is very similar. Because the water has already been filtered, the filter is bypassed in de-ballasting and the water flows through the UV reactors in order to prevent regrowth of any microorganisms that were caught between processes (EPA, 1999). Advantages to this system include the fact that, once installed on a ship, the system runs on its own and is self-monitoring.

There are also new ship designs under development that remove the necessity of the conventional ballast tank. At the University of Michigan, an innovative design was developed that uses large tubes open at both ends along the length of the ship below the waterline to provide stability, eliminating the need for traditional ballast tanks. This design prevents the ship from lifting with the waves. Figure 13 illustrates this design concept.





Source: (marinebuzz.com 2015)

Figure 13. Open-ended ballast tubes.

The forward movement of the ship recycles the water, removing any possibility of transporting foreign species any great distance (Faden, 2008). This technology would completely remove any use for ballast tanks. The design even increases the efficiency of the engines onboard because of the way that the tubes deliver water to the propellers. However, it does not directly control the draft of the vessel, making it difficult to control this parameter underway.

Research and development continues to discover effective and innovative ways to stabilize vessels. Finding an alternative to seawater ballasting would alleviate costs and operational demands involved in installing and maintaining ballast water treatment systems.

The use of shipboard gray water, with or without treatment, may be appropriate as a substitute to seawater ballasting for certain ships. However, pre-treatment of gray water, ship system modifications, potential corrosion issues, stability considerations, rates of gray water generation versus rates of ballasting, and the need for modification of regulations would all need to be considered.



3 CORROSION EXPERIMENT MATERIALS AND METHODS

3.1 Materials

3.1.1 Simulated Gray Water and Seawater Recipes

An experimental gray water recipe was developed based on input from research conducted on typical gray water produced on cruise ships (EPA, 2008). The recipe includes different constituents that make up actual shipboard gray water such as soaps, food products, personal hygiene products and laundry detergents. The recipe is summarized in Table 1 for a 5-gallon batch. A total of 25 gallons was produced at the same time for the corrosion experiment to ensure uniformity in starting conditions. Treated gray water was simulated by diluting the untreated gray water 90% by volume. Simulated seawater was mixed in the laboratory to eliminate unknown constituents and to ensure uniformity. For the production of standardized seawater, ASTM D1141 – 98(2013) was followed; however, no heavy metals were used in this study (Table 2).

Ingredient:	Units	Recipe Amount:
shower water	Gallons	1
toothpaste	Gram	0.3
shaving cream	Gram	0.05
all purpose cleaner	mL	1
anti-bacterial soap	mL	1
laundry detergent	Gram	1.75
cleanser	Gram	1.5
orange juice	mL	5
cooking oil	mL	0.5
coffee grounds	Gram	0.125
vegetable juice mix	mL	12.5
fruit juice mix	mL	12.5
choc cakes	Gram	12.5
sirloin burger soup	mL	25
tap water	Gallons	as needed to fill

Table 1.	Simulated gray water	recipe.
	Source: (EPA, 2008)	



Compound	Concentration, g/L
NaCl	24.53
MgCl ₂	5.20
Na ₂ SO ₄	4.09
CaCl ₂	1.16
KCI	0.695
NaHCO ₃	0.201
KBr	0.101
H ₃ BO ₃	0.027
SrCl ₂	0.025
NaF	0.003

Table 2. Simulated seawater recipe. Source: (ASTM, 2013)

3.1.2 Mass Loss Experiment Materials List

The materials used in the mass loss experiment are listed below in Table 3.

Table 3. Mass-loss materials list.

Product	Quantity
Steel Plate (2'x4') [cut into 1"x1"coupons]	1
1 Gal Epoxy Coating	1
400 ml Glass Beaker (48 per case)	1
20L Seawater	2
Cutting and Sandblasting	N/A
Parafilm	1
Lab Testing	N/A
1/2" x 10 ft PVC Piping	1

3.1.3 Electrochemical Analysis Materials List

The electrochemical test used the same batch of cut steel plate coupons and additional materials used in the electrochemical tests are listed below:

- 1L 3-electrode corrosion cell
- Julabo F25 Temperature monitoring system
- Pine WaveDriver 10 potentiostat
- 5 epoxy coated steel coupon samples with attached copper leads



3.2 Methods

3.2.1 Mass Loss Experiment

3.2.1.1 Metal Preparation Procedure

Six strips of A36 medium carbon steel, 1" wide by 24" long were sandblasted for five to ten minutes until a white metal finish was obtained. This removed the protective coating from the factory. Testex brand tape was used to check the surface profile of the metal. The Testex was placed on the surface of the metal then gently rubbed with a blunt object such as a pen. Care had to be taken to avoid ripping the tape. The tape was then peeled off the metal and the compression was measured with a micrometer. The steel was cut with a horizontal band saw. Coupons measuring 1" by 1" were produced. A deburring tool was used to remove the burr left by the band saw. Coupons were weighed and labeled 1 to 140 with an indelible marker.

3.2.1.2 Metal Coating Procedure

Coupons numbered 1 through 45 were brought to a paint spray booth and arranged in numerical order on a piece of cardboard. To create an intentional "holiday" exposing the metal surface, a ¹/₄ inch diameter foam dot was affixed to each coupon. The two-part epoxy was mixed together using a 1:3 ratio. After the marine epoxy was mixed, paint thinner was added to mix the marine epoxy to prevent clogging the spray gun. The samples were sprayed to obtain an even coating on the exposed face and sides. Samples were left to dry until the epoxy was slightly tacky. The samples were rotated and the spray process was repeated on the other face and allowed to dry overnight. The foam dots were removed, any residual glue remaining from the dot was removed with methanol, and any exposed metals on the sides of the coupons were hand painted with epoxy using a small foam brush.

3.2.1.3 Procedure for Mixing Simulated Gray Water, Seawater, and Mixtures

Once the materials from the recipe were obtained, the gray water was mixed in a large trash can. All components except the shower water were mixed in a blender. The blender ensured a consistent product. The blended constituents were mixed manually with the shower water in the trash can using a large stirrer. The process was repeated until the 25 gallons of gray water was produced. The trash can was covered.

The contents were thoroughly mixed to ensure uniform gray water in each beaker and to obtain samples to send to a nearby testing lab for an initial analysis. Once the seawater was mixed according to the ASTM procedure, samples of seawater were obtained for analysis and to fill the mass loss beakers. Well mixed gray water and seawater were blended in additional containers to obtain a 25%/75% mixture of gray water to seawater.

3.2.1.4 Mass Loss Experiment Setup Procedure

Thirty 300 mL beakers were labeled as coated or uncoated, humid, cycled, or submerged and by water type. PVC piping, used to house coupons for the humid samples, was cut using a horizontal band saw in roughly 1-1/2" high rings. Three sections of PVC pipe (numbered 1-3) were placed in each beaker. One coupon was placed on each ring and then each beaker was filled with test water either to just below the coupon (humid condition) or to completely cover the coupons (submerged and cycled condition). The top of the beakers were covered with parafilm and placed gently in the incubator. The incubator was set for 35°C. Cycled beakers were emptied to just below the coupon level and then re-filled on a weekly cycle. Water was removed using a pipet until samples sat in a humid condition and then refilled the next week until submerged fully. Cycle water was stored in plastic bottles in the incubator after being removed.



3.2.1.5 Sample Weighing Procedure

Sensitive balance scales were used to measure the weights of coupons before and after the mass loss experiment. The environment, temperature, time of day, and other such factors were kept as constant as possible to avoid the introduction of another variable. The balance scale was placed on a granite slab to ensure that the scale remained stable. After each sample was weighed, the scale was zeroed by pressing the "tare" button.

3.2.1.6 Firecam[®] Microscopic Camera Procedure

Firecam[®] software was downloaded onto a laptop computer. The microscope was connected to a power outlet and to the computer using a USB cable. The microscope was turned on and the sample placed on the slide. Pictures were taken of each coupon using the shutter button and images were saved to the computer.

3.2.1.7 Mass Loss Experiment Disassembly Procedure

Samples were removed from the incubator. Using both a smart-phone and a Firecam[®] Microscopic camera pictures were taken of each sample. Samples were weighed while still wet, and then after hand-drying gently with a paper towel. Samples were kept in numbered plastic bags to keep track of sample IDs. To clean the samples, each coupon was placed in an ultrasonic bath for 30 minutes at approximately 50°C. Coupons were then placed in a prepared chemical solution (NaOH with Zinc) for 30-40 minutes. Then chemically treated coupons were put back in the ultrasonic-bath for 30 min at 50°C. Samples were removed from solution and hand dried. Coupons were placed back in the labeled plastic bags. The samples were reweighed. The samples were placed in a desiccator overnight for 12-18 hours to completely dry the coupons. All coupons were reweighed and final weights were recorded.

3.2.1.8 Deviation from Accepted Standards.

NACE TM0112 (NACE, 2012) is the accepted standard for a corrosion test involving ballast tank materials. Deviation from these standards was necessary due to the limited time frame and resources available. The standard specifies a 180 day test; however, due to time constraints the mass loss experiment duration was set at 50 days. The sample sizes were also smaller than that specified in the NACE standard. Coupons were 1"x1" instead of the standard's 6"x4". The smaller and lighter coupons allowed for the use of sensitive balance scales to help measure mass loss over the shorter time period. The scribe method was also altered. The scribe in the standard is done with a knife-like instrument. This method was not feasible because of the use of both electrochemical and mass loss testing. For electrochemical testing, the scribe area had to be exactly known and repeatable between coupons. A foam dot with a known diameter was attached to the metal coupon and peeled off after spraying with the epoxy coating to create a holiday of known area.

3.2.1.9 Analysis of Test Water Before and After the Experiment

After preparing the simulated seawater, simulated gray water, treated gray water, and mixtures of gray water and seawater, samples were sent to the nearby analytical lab. At the conclusion of the mass loss experiment, the beaker water used in the testing was analyzed. Parameters analyzed included BOD₅, Chemical Oxygen Demand (COD), Total Kjeldahl Nitrogen (TKN), ammonia-nitrogen, nitrate-nitrogen, nitrite-nitrogen, total phosphorous as P (TP), TSS, alkalinity, total iron, total copper, total manganese, sulfide, sulfate, coliform (total and fecal), and pH.

3.2.1.10 Procedure for Setting Up and Testing the Electrochemical Cell

The coated and scribed metal coupons used for the electrochemical tests were identical to those used in the mass loss. All electrochemical experiments were run in the fully submerged condition, because


Vessel Generated Ballast Water; Gray Water Investigation

electrochemical methods require a conductive solution to carry charge. The preparation of experimental metal coupons began by choosing a variety of metals commonly used in marine construction to later generate a reactivity series in seawater. For the initial tests three coupons of each metal (A36 steel, 6061 aluminum, and brass) were cut via band saw to the dimensions of $\frac{1}{2} \times \frac{1}{4} \times 1-\frac{1}{2}$ inches. A groove was cut at the top end of each coupon so copper wire could be attached and epoxy sealed to prevent contact with the water (Figure 14). The remaining exposed surface area for each sample was obtained and an average surface area per metal type was found to be 10 cm². These precise area measurements and epoxy coating ensured that any current pushed through the copper wire and into the metal coupon would be insulated from the water and that the only metal being corroded would be the metal coupon and not the attached copper wire.



Figure 14. Original coupon construction (from left to right): A36 steel, brass, and aluminum with attached copper wire sealed in epoxy

After the coupons were constructed, their surfaces were prepped before being placed into the 3-electrode corrosion cell (Figure 15). The prepared coupons were wiped clean and rinsed with isopropyl alcohol (IPA). After being cleansed, the coupon surfaces were polished with 600 grit emery paper to expose bright metal and then washed again with IPA. The metal samples were dried overnight. Upon testing, the coupons were suspended in the cell with only the exposed coupon surface submerged.





Figure 15. Pine Instruments 3-electrode 1L corrosion cell.

After connecting the silver/silver-chloride (Ag/AgCl) reference electrode, graphite current electrode, and prepped metal coupon as the working electrode an open-current potential (OCP) was established for the metal coupon. The OCP serves as the starting potential for both a cathodic and anodic sweep, which was performed on the three types of metals. The equilibrium potential assumed by the metal simply resting in the solution is the OCP. The OCP was established by allowing sufficient time for the OCP to stabilize before beginning the electrochemical sweep in potential away from OCP. This is because it is imperative that the system being studied has reached "steady state" and that the naturally occurring corrosion reactions of the metal sample with the reference electrode have also assumed a constant rate (Gamry, 2015). Then the cathodic and anodic sweeps were conducted by changing (adding or removing electrons into the coupon respectively) the measured voltage away from OCP by \pm 180 millivolts. The range of \pm 180 mV is standard practice for gathering current data in amps that allow for Tafel Plot analysis (a log-plot of current (i) versus overpotential). At higher overpotential, the log(i) data becomes linear. The trendlines for the cathodic and anodic region intersect at the OCP. This intersection with respect to current is known as the corrosion current (i_{corr}). The corrosion current per surface area of exposed metal can be correlated directly to mass loss measurements using Faraday's Law. Figure 16 shows a typical Tafel Plot for A36 steel in simulated ocean water.





Figure 16. Tafel Plot of A36 steel in simulated ocean water.

The lines on the Tafel plot are used to derive a slope and intercept that best fits the cathodic and anodic curves. The slope and subsequent intersection point were used to determine the corrosion rate for the coupon in the solution. Once the area of the coupon is also accounted for, a standard corrosion rate for the general metal type is determined and then compared to other metals to build an experimentally determined reactivity series of submerged marine metals and the mass loss (corrosion-doctors.org, 2015).

From the analysis of the anodic and cathodic sweeps a mass loss table, graph and a reactivity series was generated as shown in Table 4.

Metal Nobility	Mass Loss (g/m ² per day)	Process explaining deviation from Nobility	
Brass (Cu, Zn)	4.23	De-zincification	
A36 Steel	2.87	Rust formation	
AI 6061 aluminum	0.52	Protective patina	

In theory, as the nobility of a metal increases the corrosion rate should decrease. By comparing experimental values to known values, specific metals and coatings can be recommended for ships; however, corrosion resistance is only one factor, and concerns such as cost, strength and durability often drive material selection. For a standard oceanic salt-water environment of the three metals tested Al-6061 outperformed brass and A36 steel in corrosive resistance only diminishing in mass at a rate of 0.52 g/m²/day (Figure 17). This was largely due to the formation of aluminum oxide at the surface of the metal. A36 steel corroded at a



rate of 2.87 g/m²/day, while brass had a rate of 4.23 g/m²/day due to the dezincification process found when the metal is subject to submerged saline conditions.



Figure 17. Comparative corrosion rates of Brass, A36 and Al 6061 in seawater

The results shown in Figure 17 deviate significantly from the classic galvanic series shown in Figure 7 and indicate how the local environment and surface area at the coupon's surface determines how reactive a metal is to corrosion processes. Aluminum readily forms a protective oxide layer that prevents exposure of Al metal interior to the oxide from interacting with the solution at the surface of the metal. A36 steel forms an iron hydroxide film on the surface; however, this iron-hydroxide layer is porous and allows water to continue to interact and corrode interior iron metal. The zinc in the brass sample readily reacts as no protective layer is formed between the zinc and seawater solution; as a result, the corrosion rate for brass is very high as zinc readily corrodes in solution.

The following section describes the set up for the experimental apparatus (Pine "WaveDriver 10" potentiostat) and illustrates how electrochemical corrosion experiments were conducted.

3.2.1.11 Setting Up the Corrosion Cell

- Fill the cell with 1L of desired water.
- Turn on the Julabo F25 temperature monitoring system. Insert temperature probe and warm environment to 35.00°C.
- Insert standard carbon electrode to capture current.
- Insert Ag/AgCl reference electrode. Ensure no air bubbles are present in the inner cell or in reference salt bridge.
- Connect the monitoring wires from the Pine Wave Driver 10 to the cell electrodes and working sample:



- Main wire cluster secured to Pine WaveDriver 10
- Black Clip: Ground connected to any grounded metal source
- Green Clip: Attach to the carbon electrode
- Orange Clip: Insert the clip into the back of the red clip
- Red Clip: Red with orange clip attached to the working sample
- Plug wave driver USB into computer and turn on wave driver.

3.2.1.12 Running Anodic and Cathodic Sweeps

Open Aftermath software and select the following: File, New Archive Experiment → Open Current Potential (OCP) With Parameters: Induction Duration: 3 sec Electrolysis Duration: 10min Relaxation Duration: 5 sec Electrode Range Units in mV Click Audit to ensure proper parameters. Click Preform and allow system to reach an OCP equilibrium Begin Cathodic Sweep: Experiment → Linear Sweep Voltammetry at 1 mV/sec Initial Potential=OCP reading from step 5 Final Potential= - 180mV from OCP Audit then preform test

Repeat steps 3 to 5 to identify a new OCP equilibrium Begin Anodic Sweep: Experiment → Linear Sweep Voltammetry at 1 mV/sec Initial Potential=OCP reading from step 7 Final Potential= +180mV from OCP Audit then preform test Perform the OCP, Cathodic, and Anodic tests three times each



4 ALTERNATIVE METHODS

4.1 Sample Preparation Alternatives

Initially, there was significant discussion concerning the best size to use for the mass loss coupon as well the method of coupon preparation. The NACE standards call for 6" by 4" samples that when coated, are scribed with a sharp tool in a straight line measuring about 4" down the length of the sample. Following the 2014 capstone project where the samples were too heavy to use the sensitive balance for mass loss, smaller coupons were chosen for this study that would be compatible with the sensitive scale.

Methods considered for cutting out the samples from a larger sheet of A36 steel included contracting to an outside company, plasma jet cutting, and utilizing a band saw. Initially the plasma cutter was selected due to the ease of use, accuracy of samples, and lack of cost for contracting. Initial coupons cut had severe edge damage and a large heat affected zone, which would present an additional variable in the corrosion process. The decision was made to create coupons using a band saw, and to increase the sample size to 1" by 1" for easier cutting. This method eliminated edge damage aside from an easily removed burr, and did no damage to the sample face. All coupons used in the experiment were produced by the band saw method.

4.2 Alternatives for Prepping Samples at the end of the Mass Loss Experiment

There were several methods discussed to remove rust and dry the samples for a final weight. The two different alternatives included using a desiccator to remove moisture and using methanol. Methanol was selected; however when the final weights were taken several coupons had actually gained weight, meaning that the methanol had not been successful in the total removal of water. Upon placement in a desiccator overnight, the samples showed a mass loss.

4.3 Cruise Ship Selection Alternatives for the Feasibility Analysis

Several companies that operate large and small cruise ships were contacted for information on ship systems and operating practices to conduct a feasibility analysis of gray water ballasting. The M/V Norwegian Breakaway class was selected as a model ship, due to the willingness of the company to share drawings, information on ship operations, and ballasting/wastewater practices. The company also hosted the capstone team for a tour of the ship and ship engineers and operators were available to answer questions. Other companies, including several smaller cruise ship companies, were contacted but noted that their operating procedures and practices did not regularly include ballasting, nor provided the detailed type of information needed to include them in feasibility assessments. Therefore, the feasibility study focused on the Norwegian Breakaway.



5 **RESULTS AND DISCUSSIONS**

5.1 Mass Loss Corrosion Experiment Results

5.1.1 Quantitative Results

5.1.1.1 Mass Loss Data and Discussion

Mass loss data were analyzed in mass (g) and in rate of mass loss $(g/m^2/day)$ which was obtained by dividing mass loss by exposed surface area and duration of the experiment (50 days). For the coated and scribed coupons, the surface area was easily calculated from the $\frac{1}{4}$ inch foam dot used to make the holiday. Due to inconsistencies in the size of the coupons, the exposed area for the uncoated coupons was estimated from approximate dimensions. The mass loss data in grams are presented in Appendix A. Figure 18 and Figure 19 show the mass loss average in $g/m^2/day$ for the coated / scribed samples and uncoated samples, respectively based on coupon exposure scenario (humid, cycled, and submerged) and water type.



Figure 18. Mass loss for coated/scribed samples (average of replicates).





Figure 19. Mass loss for uncoated samples (average of replicates).

Of the three environments simulated, the most corrosive environment was the cycled wet/dry sample for most water types. The cycled tank environment simulates the tidal splash zone above the water level, as shown in Figure 20. In this zone, the samples are exposed to abundant amounts of both oxygen and water; which means that there is no limiting reactant to the corrosion reactions.





Figure 20. Relative loss in metal thickness based on depth in water.



Vessel Generated Ballast Water; Gray Water Investigation

A comparison of corrosion rates for seawater and untreated gray water for the coated/scribed samples show a greater corrosion rate for seawater in the submerged state and a greater corrosion rate for gray water in the humid and cycled conditions. There may be a reaction occurring with gray water corrosion that depends on having a supply of oxygen. For the uncoated samples, overall mass loss rates $(g/m^2/day)$ were lower indicating that the epoxy/scribe interface experienced accelerated corrosion. This was confirmed by visual inspection under the microscope which revealed evidence of crevice and pitting type corrosion. For the uncoated samples, seawater resulted in greater corrosion rates compared with untreated and treated gray water in all exposure scenarios. The different trends for coated/scribed and uncoated samples are difficult to explain based on the data collected. The trends for the gray water and seawater mixtures were inconsistent and present a complex situation compared with untreated gray water and seawater alone.

The formation and deterioration of surface films likely contribute to the inconsistent results as biological activity was present in the mixtures; however, further study would be required to account for the extent and influence of surface film formation. BOD₅ was measured at the start of the mass loss experiment and at various time intervals from samples taken from a control beaker in the incubator that did not hold coupons. As can be seen in Figure 21, significant biological degradation occurred for the gray water over time in the incubator. The biological activity in the gray water could have affected corrosion rates by introducing some form of biological corrosion or corrosion inhibition due to a biofilm. The biological reactions also could affect solution chemistry which in turn could have affected corrosion rates. A more comprehensive study of potential biological reaction affects on corrosion would be needed to better understand the impact.



Figure 21. BOD₅ decline over time for gray water in the mass loss incubator.

Analysis of the corrosion water before and after the mass loss experiment was used to help explain some of the corrosion and mass loss data observed and to better understand the potential role of biodegradation of the gray water and solution chemistry on corrosion rates. Table 5 and Table 6 show the composition of corrosion water before and after the mass loss test for the coated/scribed samples and for the uncoated samples respectively. Appendix II contains initial water analysis for the mass loss and the electrochemical experiments.



Sample	BOD₅ mg/L	COD mg/L	рН	Alkalinity mg/L as	lron mg/L	Manganese mg/L
				CaCO ₃		
Initial Gray Water	729	1310	5.5	51.5	0.30	0.05
Grav Water	6	324	8.63	168.1	0.62	0.14
Humid	-	-				-
Gray Water	13	210	8.00	123.4	7.85	0.26
Cycled						
Gray Water Submerged	59	520	7.69	157.9	5.38	0.21
Initial	3	170	7.99	203.8	0.03	0.06
Seawater						
Seawater Humid	8	238	8.46	227.8	1.18	0.16
Seawater	4	240	7.74	112	25.8	0.70
Cycled						
Seawater	1	180	7.91	86.8	5.44	0.40
Submerged	10	100	0.07	00.0	0.40	0.00
Initial Treated CW	46	120	6.97	62.0	0.16	0.02
Treated GW	1	21	0.25	105	0.42	0.11
Humid	4	51	0.55	105	0.45	0.11
Treated GW	7	51	7 35	53.8	3 66	0.18
Cycled	-	•			0.00	
Treated GW	5	35	7.52	56.4	1.82	0.19
Submerged						
Initial	143	310	6.98	168.4	0.37	0.08
25GW:75SW	0	000	0.05	205	0.50	0.47
25GVV:75SVV	8	260	8.25	205	0.58	0.17
2501//2581	8	160	8 1 2	120.5	0.60	0.30
Cycled	0	100	0.12	129.5	9.09	0.59
25GW-75SW	4	220	8 11	128.9	2 34	0.33
Submerged	•		0.11	12010	2.01	0.00
Initial	344	640	6.24	94.2	0.34	0.06
75GW:25SW						
75GW:25SW	14	303	8.55	209.9	0.72	0.17
Humid						
75GW:25SW	6	180	8.17	139.5	19.6	0.38
Cycled						
75GW:25SW	5	260	8.52	174.9	6.81	0.30
Submerged		1				1

Table 5. Initial and final composition of mass loss test water for coated/scribed samples.

GW = gray water

25 GW:75 SW = 25% gray water and 75% seawater 75 GW:25 SW = 75% gray water and 25% seawater



Sample	BOD₅ mg/L	COD mg/L	рН	Alkalinity mg/L as CaCO ₃	lron mg/L	Manganese mg/L
Initial Gray Water	729	1310	5.5	51.5	0.30	0.05
Gray Water Humid	13	104	7.22	88.0	42.0	0.75
Gray Water Cycled	21	139	6.99	71.3	59.8	1.26
Gray Water Submerged	23	100	7.87	125.1	5.89	0.15
Initial Seawater	3	170	7.99	203.8	0.03	0.06
Seawater Humid	22	170	4.35	40.9	571	6.71
Seawater Cycled	12	140	4.65	20.2	224	5.60
Seawater Submerged	3	120	7.64	76.0	279	3.68
Initial Treated GW	46	120	6.97	62.0	0.16	0.02
Treated GW Humid	7	14	6.76	53.5	31.9	1.55
Treated GW Cycled	4	21	4.95	28.4	59.3	5.78
Treated GW Submerged	7	14	7.21	57.3	23.2	1.62
Initial 25GW:75SW	143	310	6.98	168.4	0.37	0.08
25GW:75SW Humid	20	160	4.68	39.5	544	6.73
25GW:75SW Cycled	12	200	4.75	28.7	301	4.26
25GW:75SW Submerged	6	80	7.77	87.7	182	2.47
Initial 75GW:25SW	344	640	6.24	94.2	0.34	0.06
75GW:25SW Humid	29	132	4.47	35.1	514	4.87
75GW:25SW Cycled	80	165	4.84	26.9	340	6.43
75GW:25SW Submerged	5	15	7.43	61.1	82.8	1.12

Table 6. Initial and final composition of mass loss test water for uncoated samples.

GW = gray water

25 GW: 75 SW = 25% gray water and 75% seawater

75 GW:25 SW = 75% gray water and 25% seawater

Initial pH values ranged from 5.5 for untreated gray water to 7.99 for the initial seawater samples. For the coated/scribed samples in the untreated gray water, the pH increased from 5.5 to between 7.69 and 8.63 and the alkalinity also increased markedly over the course of the experiment. There is no obvious explanation, but it is noted that significant biological degradation took place with a significant drop in BOD₅ (greater



than 90% decrease) by the end of the mass loss experiment. Although final nitrogen analysis was not conducted, it is likely that nitrification and possibly denitrification had occurred in the beakers. Further study would be needed to determine if nitrogen reactions caused the rise in pH. The pH also rose, however, less significantly for the treated gray water and the mixtures of gray water with seawater for the coated/scribed samples.

As shown in Table 6, for the uncoated samples, there was a precipitous drop in pH over the course of the mass loss experiment for seawater in humid and cycled environments (pH decreased from 7.99 to 4.35 and 4.65 for humid and cycled samples, respectively). Similar decreases in pH were noted for seawater / gray water mixed solutions in the humid and cycled environments, but not for untreated gray water samples. While the exact mechanism for the pH drop is unknown, it appears to have occurred only for humid and cycled conditions with water containing seawater, indicating that a supply of oxygen was needed for the reaction. The pH drop led to an increased solubilization of iron and manganese as shown in the water analysis. Once the pH dropped, the coupons would be expected to have an increase in corrosion rate. The seawater and gray water/seawater mixtures with uncoated samples experienced high corrosion rates and precipitous pH drops. The same pattern did not hold for the seawater and mixtures in humid environments where the lower final pH did not appear to accelerate corrosion greatly (Figure 19). Since low final pH did not correspond with the greatest mass loss in all cases, there appear to be additional factors influencing corrosion. It is possible that microbially-mediated reactions affected both solution chemistry and corrosion rates, however, the study did not analyze this effect.

5.1.2 Qualitative Results

Qualitative results focused on the visual signs of corrosion. Samples were placed under a microscope to obtain a clearer picture of concentrated areas of corrosion in the coupons. Appendices C and D contain microscopic images and images of whole coupons taken with a smart-phone camera at the conclusion of the mass experiment, respectively.

The coated and scribed samples experienced significant corrosion around the scribed holiday. The coating performed well, limiting the corrosion to the exposed metal. Edge corrosion was also present along the edges of the coating, and some of the epoxy was found to have bubbled and flaked around the exposed metal.

The samples that experienced the least overall effects from corrosion were the humid condition. They did, however, experience some pitting that could cause damage to a ballast tank over time. The submerged and cycled coupons experienced significant corrosion. The submerged experienced more of a bubble of rust that grew steadily over the course of the experiment. The cycled samples had the greatest overall corrosion as evidenced by the higher mass loss data.

Similar to the coated samples, the uncoated coupons also presented visual corrosion results based more on environment than water type. The humid samples were again found to be the least corroded. The cycled and submerged, however, produced excessive corrosion.

The visual data collected supports the SOLAS II-1/3-2 regulations that require ballast coatings onboard vessels produced after 2008. Without coatings, the tanks would be subjected to excessive corrosion regardless of what water type was used in the tank. However, the results also indicate that serious corrosion issues may arise when the coating is breached in a ballast tank.



5.2 Electrochemical Corrosion Results

Mass loss values were determined by taking the slope and subsequent y-intercept of the Tafel plots presented in Appendix E. These Tafel plots are the results of graphing the log of the current (log i) values versus the overpotential experimentally determined through the cathodic and anodic sweeps of the metal samples. Figure 22 is a plot of the corrosion rates for each water type submerged and subject to electrochemical testing for coated/scribed A36 coupons identical to those used in the mass loss study.



Figure 22. Electrochemical corrosion rate for coated/scribed coupons by water type.

Overall, for the electrochemical corrosion process, the mixtures of gray water and seawater had the lowest rates of corrosion, while the seawater experienced the highest corrosion rate. The untreated gray water had a lower corrosion rate as compared with the seawater and the treated gray water.

Table 7 summarizes the corrosion rate for each type of water submerged in solution for the electrochemical test. Electrochemical testing was only performed on coated/scribed samples in the submerged environment and on uncorroded coupons. Electrochemical testing requires samples be in contact with a water solution (submerged) to obtain useful data.

Water Type	Rate (g/m²/day)
75% Gray water/25 %Seawater	6.2
25% Gray water/75 %Seawater	11.4
Gray water	12.3
90:10 Dilution (Treated Gray water)	18.3
Seawater	21.0

Table 7. Electrochemical corrosion rates by water type.



Through analysis of the corrosion rates of A36 steel in various water environments, a definitive answer could not be reached as to which environment is best to prevent tank corrosion but a general trend was observed. In order of most to least corrosive; seawater, treated gray water, untreated gray water, 25% gray water, and finally 75% gray water. Based on theory and on the mass loss results for the coated/scribed samples, the seawater had higher corrosion rates compared with the untreated gray water. It is unclear why the mixtures of gray water and seawater had the lowest corrosion rates.

5.3 Comparison of Mass Loss and Electrochemical Experiments

The differences between the results of the two experiments are shown in Table 8. Note that the only comparison can be for the *submerged* condition (the only condition possible for the electrochemical corrosion). The rates of corrosion were significantly higher in the electrochemical testing, with the electrochemical results ranging from 2.95 to 5.25 times higher than the mass loss results. It is possible that with future testing a predictive model could be developed to exptrapolate long term corrosion from short term electrochemical testing. The consistently higher corrosion rates for the electrochemical tests could reflect an initially higher corrosion rate which declines over time as protective films or metal oxides form on the metal. The electrochemical tests were performed on clean bright metal. Future tests could investigate electrochemical tests on samples that had already undergone some corrosion. The Tafel plots in Appendix E demonstrate a slight decrease in corrosion rate even over the course of several hours when tests were conducted consecutively in triplicate on the same sample.

	Mass-loss Ex	periment (g/m ² /day)	Electrochem (g/m ² /day)	ical Analysis	Ratio of Electrochemical: Mass Loss Rate
Water Type	Average	Standard Deviation	Average	Standard	
	Corrosion		Corrosion	Deviation	
	Rate		Rate		
Seawater	4.0	* Number of replicates	21	± 3.23e-07	5.25
Treated Gray		was too small for a			
Water	4.2	meaningful standard	18.3	±3.05e-07	4.36
Gray Water	3.2	deviation.	12.3	±2.84e-07	3.84
25%Gray					2.53
Water /75%					
Seawater	4.5		11.4	±1.30e-08	
75%Gray					2.95
Water /25%					
Seawater	2.1		6.2	±1.37e-07	

Table 8. Mass loss and electrochemical results for submerged coated/scribed samples.

Since the electrochemical experiment was conducted on uncorroded coupons, the higher corrosion rate likely reflects an initial corrosion rate. In contrast, the mass loss corrosion rates are averaged rates over a 50 day testing period. Both mass loss and electrochemical tests resulted in greater rates of corrosion for seawater compared with untreated gray water for submerged coated/scribed samples. Corrosion trends for the mixtures of gray water and seawater are difficult to explain. There may be interactions involved that cannot be understood from the data collected. The greater corrosion rates for the seawater in the submerged



Vessel Generated Ballast Water; Gray Water Investigation

coated/scribed coupons are not surprising given that higher ionic concentrations can accelerate corrosion. For the untreated gray water, microbial slime layers could have helped protect the exposed surface from corrosion. While there is evidence of significant biological activity, as shown by a decrease in BOD₅ of the gray water at removal rates well above 90 % in the mass loss study, biological activity was unlikely to be a significant phenomenon during the short-term electrochemical experiments. The importance of biological reactions and microbial activity on ballast tank corrosion would require further study.

5.4 Shipboard Feasibility Analysis Results

5.4.1 Large Cruise Ship

As the corrosion study proceeded, a parallel effort examined the feasibility of ballasting with gray water using a candidate cruise ship for which data and ship plans could be collected. The theoretical possibility of ballasting exclusively with gray water was examined for the candidate ship as well as the practical application of such a system in accordance with current regulations and ship operations. The Norwegian Breakaway was chosen as the target ship due to access to the ship crew for advice, access to ship information, and a field trip to New York City to tour the ship and her systems. The theoretical aspect of the feasibility study began with ship stability calculations. The longitudinal stability of the ship was calculated for different loading conditions based on ship plans and typical cruise routes given to us by the Norwegian Breakaway crew. For the calculations, some assumptions were made based on information provided by Norwegian Breakaway staff during the site visit and email exchanges. These assumptions and given values are listed below.

5.4.1.1 Assumptions

- 1. Longitudinal Center of Flotation (LCF) is at amidships for all conditions.
- 2. The distance from the LCF to the forward and aft perpendiculars equal half of the Length Between Perpendiculars (LBP).
- 3. Tanks to consider include all ballast tanks, fuel tanks, potable water tanks, and treated wastewater tanks, as these are the tanks that will undergo the most appreciable changes.

5.4.1.2 Given Values

- 1. The LCF is referenced using Length Over All (LOA) = 162.81 m (from bow & stern)
- 2. Length Between Perpendiculars (LBP) = 300.12 m
- 3. Optimum trim is 8.0 m by the bow, 8.1 m by the stern

This information was used to calculate the trim for three common scenarios of the vessel: transiting, entering Bermuda, and leaving Bermuda. From information given by the vessel officers, the tanks were proportioned into expected percentages of liquid per tank based on each scenario. Those percentages provided a baseline for calculations as listed in Table 9.



	Transiting	Entering Bermuda	Leaving Bermuda
Ballast	*Varies	0%	100%
Fuel	*Varies	50%	50%
Potable Water	100%	100%	15%
Treated Wastewater	*Varies	0%	100%

Table 9. Loading conditions for various scenarios on the Norwegian Breakaway.

*Values vary based on weight shifts, fuel burn rates, and wastewater generation rates.

The optimum trim given by the Norwegian Breakaway officers provided a starting point to look at in each scenario. Then a vessel-loading diagram provided by Norwegian Cruise Lines was used to find the moment to alter trim one centimeter, which is the applied moment necessary to change the combined draft of the ship one centimeter (Ships & Maritime Systems Course Reader, USCGA). For entering and leaving Bermuda, weight addition/removal calculations were the main focus, based on loading information given by the vessel for each type of tank. For the transit condition, weight shift calculations were the main focus, simulating the movement of treated wastewater to ballast tanks throughout the ship, as well as the burning of fuel. The weight of each tank was found using the volume of the tank multiplied by the density of the liquid being held in the tank. From there, the ship plans were used to determine the distances from the centers of each tank to the Longitudinal Center of Flotation, which is the longitudinal location that a vessel will pivot or trim about when weights are added or subtracted in the forward or aft direction (Ships & Maritime Systems Course Reader, USCGA). The equation to find the overall change in trim is as follows:

$$\delta Trim = \frac{Weight \ Added \ or \ removed \ * \ Distance \ from \ LCF}{MT1}$$

The sign of the distance from LCF depended on where the tank was located in relation to the LCF. For any tank forward of the LCF, the sign was negative; any tank aft of the LCF, the sign was positive. After the total change in trim was calculated, the value was apportioned to calculate the new trim conditions both forward and aft. The equations used for apportioning the trim are given below:

$$\delta T_F = rac{Distance\ from\ LCF\ to\ Forward\ Perpendicular}{LBP} * \delta Trim$$

 $\delta T_A = rac{Distance\ from\ LCF\ to\ Aft\ Perpendicular}{LBP} * \delta Trim$

Based on the assumptions used, the forward and aft trims calculated at this point were equal. After finding the forward and aft trims, it was a matter of using the proper sign to find the final forward and aft drafts. Table 10 contains the final values calculated.

	Transiting*	Entering Bermuda	Leaving Bermuda
Forward Draft	8.318	8.403	8.372
Aft Draft	7.782	7.697	7.728

Table 10. Final forward and aft drafts estimated for the Norwegian Breakaway

*Based on the most extreme realistic scenario



Vessel Generated Ballast Water; Gray Water Investigation

In the transit calculations, values were shifted from the treated wastewater and ballast water tanks to simulate filling the ballast tanks with treated wastewater. This was the driving condition that would prove whether or not it would be theoretically possible to ballast using gray water. The transiting value was calculated on a one-hour, six-hour, 12-hour, and 24-hour basis using the fuel burn rate and wastewater generation rate simultaneously. From the vessel staff, their fuel burn rate for a typical 7-day cruise to Bermuda is 4.76 m³/hr, and their wastewater generation rate is about 50 m³/hr. The Chief Officer also provided the fact that the forepeak (farthest forward) and skeg (farthest aft) ballast tanks were usually filled and emptied first, due to their locations on the ship and ease of making small changes to the overall trim using those tanks. Changes in trim were very slight in the one, six, and even twelve hour periods examined for different loading possibilities. When the most extreme case was taken into consideration (filling the tanks closest to the stern first while removing water from the tanks closest to the bow), appreciable changes were seen in overall trim but not quite enough to make it back to the optimum trim based on the fuel burn rate and wastewater generation rate.

The calculations show that, although theoretically possible, it would take the most extreme loading condition while transiting to begin to move toward the optimum trim of the vessel. Because the forepeak and skeg are the tanks used to trim the vessel, it would be necessary to remove fuel from as far forward as possible while moving the gray water into the farthest aft ballast tanks possible. In addition to this, other larger tanks that would affect the trim more significantly are usually kept at constant levels by the computer system aboard the Breakaway.

The other main component of the feasibility study was geared toward the practicality of a gray water to ballast tank system. Before knowing which ship was going to be visited, it was not certain what type of ballast and wastewater systems would be examined. Because the Norwegian Breakaway was recently built (2013), it contains a state of the art Advanced Wastewater Purification System (AWPS). While it is feasible to ballast with gray water, both ballast water and gray water regulations and practices would need to be reviewed to evaluate whether such a practice is desirable. For example, the technology contained on the Breakaway and her competitors has advanced past the need of putting any type of untreated gray water into ballast tanks. From our contact at Norwegian Cruise Lines, it was said that treated wastewater could also potentially be used as ballast water, which would lead to less corrosion in the tanks compared to untreated gray water. The Breakaway also includes a ballast water treatment system that runs during both ballasting and deballasting processes, and currently meets IMO ballast water discharge standards. The AWPS also treats wastewater well enough for the Breakaway to meet inport discharge standards, giving them more flexibility as to where they can discharge in cases of emergency. (Though, as a normal practice, they do not discharge treated wastewater within a country's territorial sea, i.e., within 12 nautical miles of the coast.) Finally, wastewater and ballast water regulations are treated differently by the Coast Guard, IMO, and EPA. Using untreated wastewater inside of ballast tanks presents an unclear regulatory area. Since there is no clear definition as to what constitutes ballast water, the use of gray water in a ballast tank falls into ballast water regulations by default since it is water used to control the trim of a vessel. Further regulatory studies would have to be conducted to determine if gray water loaded into a ballast tank could be treated as gray water, which has less stringent discharge standards. Both of the Breakaway's wastewater and ballast water management processes are working as intended, so they do not currently have a need to change both shipboard systems or try to comply with mixed regulatory schemes.



5.4.2 Small Cruise Ships

Three companies that operate smaller cruise ships in the Great Lakes were contacted and all declined to participate in this study. This is understandable given the stringent regulations for gray water in the Great Lakes. For instance, Section 312 of the Clean Water Act, as defined by 33 U.S.C 1322 (a)(10), includes gray water as "sewage from vessels," and is not permitted to be discharged in US waters in the Great Lakes (No discharge zones). Also, as noted for the large cruise ship, regulatory frameworks do not exist currently to accommodate gray water ballasting, without treating gray water as ballast water.

Smaller cruise ships produce much less gray water; and having fewer amenities that produce gray water may also limit the feasibility or desirability of gray water ballasting. In addition, small cruise ships have the ability to moor every 24 to 48 hours. This gives the vessel the opportunity to hold all sewage and gray water; and pump it to a shore unit for treatment. It might also prove to be challenging on a small cruise ship to re-design systems to accommodate gray water ballasting, especially on vessels with shallow draft, relatively small (and crowded) engineering spaces, and limited footprint to allow for additional machinery and treatment system installation.

An analysis similar to the one conducted for the Norwegian Breakaway with a smaller ship could indicate whether it is actually feasible and/or desirable to ballast with gray water on small cruise ships. Given the ever-increasing discharge regulations and concern over sensitive ecosystems on the Great Lakes, alternative ballasting practices may become a more viable issue in the future.



6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions and Recommendations: Corrosion Studies

The results of the mass loss study led to the following general conclusions:

- For the coated/scribed coupons, mass loss was greater for the seawater than for the untreated gray water in the submerged environment. For the humid and cycled conditions, the mass loss was much greater for the untreated gray water. Cycled samples had the greatest mass loss. The reasons for these effects are unclear compared with the seawater.
- For the uncoated samples, mass loss was greater for the seawater samples than for the untreated gray water samples regardless of the exposure scenario (humid, cycled, and submerged). The pH of seawater and mixtures of gray water and seawater decreased from neutral to between 4 and 5 over the course of the experiment for cycled and humid samples. The cycled samples had the greatest mass loss and humid samples had the least mass loss indicating that other factors beside low pH affected corrosion rates.
- The results for the gray water / seawater mixtures were inconsistent and difficult to explain. Generally, the coupons in the treated gray water experienced mass loss between that of seawater and untreated gray water.
- Visual inspection of coupons at the conclusion of the mass loss study showed the least visual corrosion for the humid condition, which matched the mass loss results. Coupons subjected to cycled conditions appeared to have the most rust colored deposits.
- Although total mass loss was greater for uncoated samples, the rate of corrosion in g/m²/day was greater for the coated/scribed samples; and there were indications of pitting corrosion at the interface of the epoxy coating and the scribe. These types of situations might occur in ballast tanks where the coating has been compromised.

The results of the electrochemical study led to the following general conclusions:

- The rates of corrosion in g/m²/day were consistently greater for the electrochemical experiment compared with the same treatment in the mass loss study. The ratios of corrosion rates of electrochemical to mass loss data ranged from 2.95 to 5.25. This greater corrosion rate with the electrochemical experiment may reflect that the electrochemical tests represent an initial corrosion rate as these tests were conducted on polished surfaces while the mass loss experiment reflected an overall corrosion rate over the duration of a 50 day experiment.
- The rate of corrosion was greatest for seawater for both the electrochemical corrosion study and the mass loss study on coated/scribed coupons in the submerged state.

Recommendations for future corrosion studies based on the results and conclusions:

• Perform mass loss and electrochemical studies with fewer water types (seawater and gray water) to focus on the factors affecting corrosion rates and solution chemistry/biology over time.



- Examine the potential role of biological reactions and microorganisms on ballast tank corrosion with gray water.
- Examine the electrochemical experiments on steel coupons and various water types at time intervals to capture the change in corrosion rates over time as coupons corrode and as water quality changes. Target better correlation between mass loss and electrochemical studies so that electrochemical experiments can be used to predict long term corrosion rates.
- Examine other coating imperfections that might promote corrosion to include scribes, poor coating adhesion, and incomplete surface preparations. Use electrochemical impedance studies to measure the extent of corrosion.

6.2 Conclusions and Recommendations: Feasibility Study

- An analysis of the Norwegian Breakaway based on trim calculations, ship systems, ballasting practices and wastewater generation rates, indicated that gray water ballasting may be feasible on large cruise ships. However, with state-of-the-art wastewater and ballast treatment systems onboard newer ships it may not be desirable or practical to change ballasting practices on existing ships.
- Future feasibility studies should focus on small cruise ships operating in and along the Great Lakes. Many large cruise ships have evolved past the need to ballast with the gray water they produce and they operate in oceans far from shore. Older, smaller cruise ships, operating in areas of heightened environmental concern may present more of an opportunity for gray water ballasting. Challenges dealing with mixed regulatory schemes for gray water and ballast water, and difficulties in modifying smaller ships for alternative ballasting practices must be considered.
- Alternative ballasting on government vessels (e.g., Coast Guard as 225' Buoy Tenders) could be explored in future studies.

6.3 General Conclusions

The corrosion studies combined with the feasibility study indicate that gray water ballasting may be practical for ships that are seeking a solution to gray water and ballast water challenges. Large cruise ships appear ideally suited for gray water ballasting due to the large amounts of gray water produced; however, modern ships such as the Norwegian Breakaway would likely have water treatment systems designed to meet the regulatory challenges posed by wastewater and ballast water management.

The results of mass loss and electrochemical studies indicate that gray water (treated or untreated) may provide a less corrosive environment for coated ballast tanks with scratches and imperfections in the coating under fully submerged conditions. However, the untreated gray water samples experienced greater mass loss compared with seawater samples in humid and cycled environments with coated/scribed coupons. As expected, the cycled environment was most corrosive and this environment simulates conditions near the surface of ballast tanks. With additional study, short-term electrochemical experiments may be able to predict longer term corrosion when ballast tank materials are subjected to various types of water under various environmental conditions.



7 **REFERENCES**

- 33 U.S.C.1901 Note. Departments of Labor, Health and Human Services, and Education, and Related Agencies Appropriations Act, 2001, Pub. L. No. 106-554, 114 Stat. 2763, enacting into law Title XIV of Division B of H.R. 5666, 114 Stat. 2763A-315, and codified at 33 U.S.C. 1901 Note ("Title XIV"))
- American Bureau of Shipping. "Guide for Ballast Water Exchange." Houston. 2010.
- Alaska Department of Environmental Conservation (ADEC). 2012. Cruise Ship Wastewater Science Advisory Panel Preliminary Report. http://dec.alaska.gov/water/cruise ships/pdfs/SAP Preliminary Report November 2012.pdf
- Alaska Department of Environmental Conservation (ADEC). 2002. The Impact of Cruise Ship Wastewater Discharge on Alaska Waters. Juneau, AK. www.dec.state.ak.us/water/cruise_ships/pdfs/impactofcruiseship.pdf
- Alfa Laval. "PureBallast 3.0 In Detail." http://www.alfalaval.com/campaigns/pureballast3/Documents/technical.htm#basic-facts. (Dec. 9, 2014)
- American Galvanizers Association (2015) American Galvanizers Association. N.p., n.d. Web. 22 Apr. 2015. http://www.galvanizeit.org.
- ASTM. American Society of Testing and Materials. Standard Practice for the Preparation of Substitue Ocean Water (ASTM D1141 98(2013). http://compass.astm.org/EDIT/html_annot.cgi?D1141+98\(2013\)
- "Ballast Water." MITSG CCR: Marine Bioinvasions. N.p., n.d. Web. 04 May 2015 http://massbay.mit.edu/exoticspecies/ballast.
- "Ballast Free Ship Concept Being Developed by University of Michigan." MarineBuzzcom RSS. N.p., n.d. Web. 04 May 2015. http://www.marinebuzz.com/2008/03/27/ballast-free-ship-concept-being-developed-by-university-of-michigan/>.
- Bard, A. J.; Faulkner, L. R. "Electrochemical Methods. Fundamentals and Applications" 2nd Ed. Wiley, New York. 2001. ISBN 0-471-04372-9
- Boatdesign.net (2015) N.p., n.d. Web. http://www.boatdesign.net/forums/attachments/sailboats/59083d1311467587-perils-edgy-designoffshore-y-stab-1.jpg.
- Brinkley, J., Johnson, C.H., Souza, R. (2007). "Moving Bed Biofilm Reactor Technology A Full-Scale Installation for Treatment of Pharmaceutical Wastewater."
- Chase, C., Pederson, J., Reilly, C. (undated) "Ballast Water Treatment Options." Marine Bioinvasions Fact Sheet. Sea Grant. 1-4
- "Corrosion Study of Steel Structure in Seawater Chiang Yen Cathodic Protection Co.,Ltd.". N.p., n.d. Web. 04 May 2015. http://us.cycptw.com/cp3.
- Corrosion-doctors.org (2014) "Corrosion in Neutral or Alkaline Environments" http://www.corrosion-doctors.org/Chemistry-of-Corrosion/corrosion-in-neutral.htm (05DEC, 2014)
- Corrosion-doctors.org (2015) "Corrosion Rate Conversion." Corrosion Rate Conversion. N.p., n.d. Web. 22 Apr. 2015. http://www.corrosion-doctors.org/Principles/Conversion.htm



- Davis, M. and Cornwell, D. (2012) Introduction to environmental engineering, 5th Ed., McGraw-Hill, New York.
- EPA (1999). "Wastewater Technology Fact Sheet: Ultraviolet Disinfection." United States Environmental Protection Agency. Municipal Technology Branch. 1-7
- EPA (2007). "Wastewater Management Fact Sheet: Membrane Bioreactors." United States Environmental Protection Agency. 1-9
- EPA (2008). Cruise Ship Discharge Assessment Report. EPA 842-R-07-005, U.S Environmental Protection Agency, Office of Water, Washington, DC
- Evac. "ORCA III (Physical Chemical Treatment)." http://www.evac.com/product/orca-iii-physicalchemical-treatment. (Dec. 9, 2014)
- Faden, M. (2008) "Bye-Bye to Ballast Water?" Frontiers in Ecology and the Environment 6.4,175. 08 Dec. 2014.
- Gamry (2015) "Basics of Electrochemical Corrosion Measurements." Electrochemical Corrosion Measurements. N.p., n.d. Web. 22 Apr. 2015. http://www.gamry.com/application-notes/basics-of-electrochemical-corrosion-measurements/
- Gdowski, G. (1997) "Long Term Corrosion Studies" Lawrence Livermore National Laboratory https://e-reports-ext.llnl.gov/pdf/234381.pdf (05DEC, 2014)
- Gordonengland.co.uk (2015) "Corrosion." And How Thermal Spray Coatings Can Help. N.p., n.d. Web. 22 Apr. 2015. http://www.gordonengland.co.uk/corrosion.htm.
- Headworks Intl. "ActiveCell: MBBR/IFAS Wastewater Treatment." http://www.headworksinternational.com/userfiles/file/HW%20BIO%20Literature/ActiveCell%20Broch ure%20WEB%20LTR.pdf.(Dec. 9, 2014)
- Hendrix Group (2015) "Dezincification." The Hendrix Group Resources Material Property Data Copper and Copper Alloys Brasses. N.p., n.d. Web. 22 Apr. 2015. http://hghouston.com/resources/material-property-data/copper-and-copper-alloys/brasses/dezincification.aspx
- IMO (2014) "Ballast Water Management." IMO. N.p., n.d. Web. (08 Dec. 2014)
- IMO (1993) 18th Assemby IMO § 1,4-6,9 et seq. (1993) Resolution A. 774 (18).
- "Inhibiting Rust and Corrosion to Prevent Machine Failures." Inhibiting Rust and Corrosion to Prevent Machine Failures. N.p., n.d. Web. 04 May 2015. http://www.machinerylubrication.com/Read/29116/inhibiting-rust-corrosion.
- Jones, D. A. (1992) Principles and Prevention of Corrosion 1st Ed. New York, New York
- Jrn.com (2015) N.p., n.d. Web. http://media.jrn.com/images/660*413/b99289167z.1_20140611224929_000_gnu6jrdv.1-1.jpg.
- Kastenmarine.com (2015) "Metal Parts for Boats." Metal Parts for Boats. N.p., n.d. Web. 22 Apr. 2015. http://www.kastenmarine.com/metalparts.htm
- Kraft, A. (2008). "Electrochemical Water Disinfection: A Short Review." Platinum Metals Rev. 2008 52(3), 177-185



- Lee, J., Ray, R., Lemieux, E., Falster, A., Little, B,. (2004) "An Evaluation of Carbon Steel Corrosion under Stagnant Seawater Conditions" Biofouling: The Journal of Bioadhesion and Biofilm Research http://www.tandfonline.com/doi/pdf/10.1080/08927010400013274 (05DEC, 2014)
- Maritime Sun (2014) "Evac Introduces ORCA III: The Small Footprint Physicochemical Wastewater Treatment Unit." http://www.maritimesun.com/news/evac-introduces-orca-iii-the-small-footprint-physicochemical-wastewater-treatment-unit (Dec. 9, 2014)
- Minnesota Pollution Control Agency (2014) Vessel Discharge, Ballast Water Program -. (08 Dec. 2014)
- Morgenstern, L., and Pieken, D. "Cruise Lines International Association." Cruise Lines International Association. Web. (08 Dec. 2014)
- NACE TM0112-2012 (2012) "Standard Test Method: Test to Determine the Corrosion Effects of Ballast Water Treatment Systems on Ballast Tanks" National Association of Corrosion Engineers.
- National Small Flows Clearinghouse. "Explaining the Activated Sludge Process." Pipeline. 14(2), 1-7
- Ocean Conservancy (2004) "Cruise Ships and Clean Oceans" http://act.oceanconservancy.org/site/DocServer/fscruiseships.pdf?docID=102
- Paik, J. K., Thayamballi, A. K., Park, Y. I., Hwang, J. S., (2004) "A time-dependent corrosion wastage model for seawater ballast tank structures of ships" Corrosion Science.
- Pine WaveDriver 20Bipotentiostat/Galvanostat User Guide DRU10001
- RWO GmbH. "CleanBallast: The RWO Ballast Water Treatment System." http://www.rwo.de/rwo/ressources/documents/1/5272,RWO_CleanBallast_WEB.pdf (Dec. 9, 2014)
- Pillis et al., 2006 "Materials Research Effect of Rare Earth Oxide Additions on Oxidation Behavior of AISI 304L Stainless Steel." Materials Research - Effect of Rare Earth Oxide Additions on Oxidation Behavior of AISI 304L Stainless Steel. N.p., n.d. Web. 04 May 2015. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1516-14392006000400006.
- Alonso-Falleiros, N., and Wolynec, S. (1998) Effect of Niobium on Corrosion Resistance to Sulfuric Acid of 430 Ferritic Stainless Steel. Materials Research, Vol 1, n.1. Retreived 04 May 2015from http://www.scielo.br/scielo.php?pid=S1516-14391998000100007&script=sci_arttext.
- SESCO, Inc. (2015) "Cathodic Protection Engineering." SESCO, Inc. :: Cathodic Protection Engineering. N.p., n.d. Web. 22 Apr. 2015. http://www.sescocp.com/tutorial.php.
- Spross, J. (2014) "Here's What Happens To Sewage On Cruise Lines."ThinkProgress Heres What Happens To Sewage On Cruise Lines Comments. Climate Progress, (08 Dec. 2014)
- Sustarsic, M. (2009). "Wastewater Treatment: Understanding the Activated Sludge Process." CEP Magazine. AIChE. 26-29
- Vera, R., Guererro, F., Delgado, D., Araya, R. (2013). "Atmospheric Corrosion of Galvanized Steel and Precipitation Runoff from Zinc in a Marine Environment." J. of the Brazilian Chemical Society 24(3).
- Vukanic, V., Ivanovic, Z., Urosevic, V., and Ljustina, A. (2008) "Integrated Coastal Management of the Ships' Ballast Water in the Montenegrin Sea Ports." Natura Montenegrina 9.3, 499-506.
- Weisenburger, A., Schroer, C., Jianu, A., Heinzel, A., Konys, J., Steiner, H., Müller, G., Fazio, C., Gessi, A., Babayan, S., Kobzova, A., Martinelli, L., Ginestar, K., Balbaud-Célerier, F., Martín-Muñoz, F.J., Soler Crespo, L. (2011) "Long term corrosion on T91 and AISI1 316L steel in flowing lead alloy and



corrosion protection barrier development: Experiments and models" Journal of Nuclear Materials. 415(2011) 260-269.

Williams, J. R. (1996) "An Inexpensive Corrosion Laboratory Experiment." Purdue University Statewide Technology. http://fie-conference.org/fie96/papers/277.pdf.



APPENDIX A. MASS LOSS DATA

Key to All Appendix 1 tables

Material:	Water:
CS: Coated/Scribed	SW: Seawater
U: Uncoated	T: Treated Gray Water
	UT: Untreated Gray Water
Environment:	75G: 75% Gray Water, 25% Seawater
C: Cycled	25G: 25% Gray Water, 75% Seawater
H: Humid	
S: Submerged	

Table A-1. Mass Loss Data for individual test coupons.

Sample #:	Trial:	Material	Water:	Environment	Weight 1 (g)	weight 2	weight 3	Weight 4	Weight 5	Weight 6
48	1	CS	T	S	33.04912	33.48689	33.48230	test sample	Test Sample	
2	2	CS	T	S	33.50424	34.02475	34.01826	34.02411	34.01707	34.01185
3	3	CS	T	s	33.22790	33.78279	33.76653	33.76925	33.76355	33.75976
4	1	CS	T	н	34.09231	34.65585	34.64257	34.64401	34.64063	34.63833
5	2	CS	Т	н	34.47204	34.99339	34.98201	34.98437	34.97986	34.97765
6	3	CS	T	н	32.69252	33.02305	33.18750	33.18863	33.18623	33.18405
7	1	CS	Т	с	35.02152	35.67458	35.62190	35.62308	35.61614	35.61151
8	2	CS	T	С	34.35901	34.77594	34.76776	34.77572	34.76195	34.75788
9	3	CS	T	с	34.35784	34.85887	34.84865	34.85454	34.84554	34.83975
10	1	CS	UT	s	34.38129	34.90599	34.89848	34.90898	34.89261	34.88874
11	2	CS	UT	S	34.75434	35.28885	35.26234	35.27053	35.26424	35.25996
12	3	CS	UT	S	34.70762	35.22615	35.20943	35.2196	35.21054	35.20647
13	1	CS	UT	н	31.93598	32.40679	32.39209	32.39204	32.38642	32.38453
14	2	CS	UT	н	35.70196	36.19910	36.16278	test sample	Test Sample	test samples
15	3	CS	UT	н	34.82994	35.37461	35.36837	35.36726	35.36541	35.36242
16	1	CS	UT	с	35.85149	36.45606	36.44122	36.44682	36.43898	36.43085
17	2	CS	UT	с	34.22653	38.35931	38.34838	38.35893	38.33785	38.33328
18	3	CS	UT	С	37.72674	34.80452	34.78295	34.79462	34.78012	34.77593
50	1	CS	SW	S	27.73802	28.22727	28.22171	28.22864	28.22068	28.21591
20	2	CS	SW	s	37.09955	37.67636	37.66500	37.70242	37.66888	37.65530
21	3	CS	SW	s	34.59202	35.02924	35.02568	35.05366	35.03203	35.02198
22	1	CS	SW	н	27.75488	28.12348	28.12049	28.12417	28.12151	28.11912
23	2	CS	SW	н	27.26532	27.59674	27.59385	27.59797	27.59524	27.59346
24	3	CS	SW	н	34.86488	35.54245	35.50741	35.50544	35.50394	35.50122
25	1	CS	SW	с	35.01136	35.61303	35.60649	35.62273	35.60927	35.59748
46	2	CS	SW	с	34.64206	35.11135	35.10634	35.13229	35.11296	35.1001
27	3	CS	SW	с	36.61643	37.15038	37.13547	37.14626	37.13674	37.12828
28	1	CS	75 G	S	36.67152	37.26975	35.25411	37.27386	37.26149	37.25341
29	2	CS	75 G	S	28.04760	28.51743	28.50955	28.52566	28.51288	28.50788
30	3	CS	75 G	S	35.32248	35.88265	35.87382	35.88706	35.87285	35.86879
31	1	CS	75 G	н	35.14832	35.66634	35.65500	35.65535	35.65458	35.65249
32	2	CS	75 G	н	34.11982	34.82361	34.81135	34.81062	34.80783	34.80500
33	3	CS	75 G	н	34.38936	34.89034	34.86993	test sample	Test Sample	test samples
49	1	CS	75 G	С	32.56310	33.08435	33.07169	33.10992	33.08773	33.07193
35	2	CS	75 G	C	34.97074	35.42796	35.41936	35.4435	35.42907	35.42128
36	3	CS	75 G	С	32.90044	33.34933	33.34498	33.35983	33.34737	33.3429
37	1	CS	25 G	s	33.15499	33.85172	33.84090	33.85937	33.84355	33.83231
38	2	CS	25 G	S	34.66270	35.27621	35.26028	35.29073	35.26856	35.25348
39	3	CS	25 G	S	35.85664	36.37863	36.37083	36.38968	36.37345	36.36498
40	1	CS	25 G	н	33.89689	34.43531	34.42214	34.42222	34.42002	34.41804
41	2	CS	25 G	н	35.91805	36.46806	36.45745	36.45839	36.45579	36.45385
47	3	CS	25 G	н	34.79064	35.32019	35.31269	35.31227	35.31145	35.30959
43	1	CS	25 G	с	35.41892	35.94094	35.93238	35.96017	35.93981	35.92365
44	2	CS	25 G	с	37.50279	38.20825	38.19429	38.21208	38.19273	38.18277
45	3	CS	25 G	С	35.19223	35.67849	35.67203	35.69135	35.67192	35.66246



Sample #:	Trial:	Material	Water:	Environment	Weight 1 (g)	weight 2	weight 3	Weight 4	Weight 5	Weight 6
51	1	U	Т	S	33.16212	33.16202	33.16202	33.16671	33.04917	33.04869
52	2	U	Т	s	27.22491	27.22471	27.22460	27.17854	27.15519	27.15507
53	3	U	Т	s	27.05147	27.05136	27.05131	26.97338	26.96603	26.96562
54	1	U	Т	н	25.46875	25.46846	25.46856	25.47057	25.46445	
55	2	U	Т	н	27.08256	27.08235	27.08220	27.08351	27.07836	27.07824
56	3	U	Т	н	28.03112	28.03126	28.03091	27.99797	27.96933	27.96828
57	1	U	Т	с	27.54362	27.54339	27.54316	27.60115	27.23427	27.23141
58	2	U	Т	с	27.35009	27.34992	27.35024	27.32496	27.47699	27.47457
59	3	U	Т	с	27.72767	27.72750	27.72784	27.92753	27.69468	27.68234
60	1	U	UT	S	34.59344	34.59332	34.59314	34.59055	34.57367	34.57365
61	2	U	UT	S	33.03484	33.03500	33.03474	33.02526	33.00673	33.00648
62	3	U	UT	S	33.25669	33.25649	33.25667	33.24947	33.2269	33.22675
63	1	U	UT	н	36.21530	36.21502	36.21510	36.25584	36.16019	36.15949
64	2	U	UT	н	32.49519	32.49502	32.49515	32.49855	32.4534	32.45032
65	3	U	UT	н	33.63765	33.63775	33.63788	33.67218	33.57737	33.57601
66	1	U	UT	с	33.37687	33.37672	33.37679	33.46767	33.32169	33.3181
67	2	U	UT	с	32.61186	32.61174	32.61149	32.73162	32.63611	32.62809
68	3	U	UT	с	32.72000	32.71986	32.71997	32.83682	32.71447	32.70012
69	1	U	SW	S	32.62042	32.62034	32.62051	32.599	32.48553	32.48542
70	2	U	SW	S	32.71468	32.71469	32.71441	32.53332	32.57763	31.5797
71	3	U	SW	S	33.04274	33.04246	33.04275	32.9366	32.8996	32.8413
72	1	U	SW	н	32.41562	32.41492	32.41474	32.41109	32.39859	33.14346
73	2	U	SW	н	35.60620	35.60583	35.60574	35.61655	35.59603	32.57777
74	3	U	SW	н	35.77244	35.77227	35.77239	35.69681	35.59833	32.89914
75	1	U	SW	С	31.89079	31.89062	31.89059	31.95384	31.41193	32.39838
76	2	U	SW	с	32.33467	32.33455	32.33442	32.25051	31.91445	35.59459
77	3	U	SW	с	32.06546	32.06529	32.06531	31.97173	31.58281	35.59782
78	1	U	75 G	S	32.93833	32.93799	32.93818	32.91579	32.84148	31.39795
79	2	U	75 G	S	35.97906	35.97865	35.97887	35.92635	35.88541	31.91117
80	3	U	75 G	S	33.10144	33.10119	33.10113	33.06849	33.01118	33.01061
81	1	U	75 G	н	33.46576	33.46564	33.46579	33.45751	33.39541	35.88502
82	2	U	75 G	н	33.30665	33.30627	33.30632	33.30993	33.2954	33.39077
83	3	U	75 G	н	35.93865	35.93778	35.93804	35.80468	35.73644	33.29498
84	1	U	75 G	С	32.75355	32.75326	32.75341	32.74619	32.59027	35.73536
85	2	U	75 G	С	30.82795	30.82777	30.82820	31.06897	30.56216	30.55236
86	3	U	75 G	С	33.06692	33.06661	33.06649	33.21414	32.71575	32.58605
87	1	U	25 G	S	32.82691	32.82682	32.82682	32.73091	33.14396	32.71532
88	2	U	25 G	s	33.26096	33.26048	33.26062	33.20306	32.74546	32.74217
89	3	U	25 G	S	33.96025	33.95982	33.96010	33.87768	33.85667	33.85643
90	1	U	25 G	н	26.97824	26.97804	26.97797	27.00973	26.90991	26.90950
91	2	U	25 G	Н	32.82624	32.82575	32.82563	32.83115	32.46972	32.45693
92	3	U	25 G	н	34.58789	34.58743	34.58790	34.53939	34.48727	34.48583
93	1	U	25 G	С	32.21758	32.21722	32.21736	32.3839	31.68434	31.68255
94	2	U	25 G	С	34.04163	34.04101	34.04095	33.93026	33.52201	33.52012
95	3	U	25 G	с	32.26368	32.26344	32.26303	32.47883	31.66291	31.65609

Table A-1. Mass Loss Data for individual test coupons (continued).



Material	Water:	Environment	Mass Loss average (g)	Standard Deviation:
CS	Т	S	0.00659	0.000254558
CS	Т	Н	0.004016667	0.000494402
CS	Т	С	0.009723333	0.000757254
CS	UT	S	0.005026667	0.004092155
CS	UT	Н	0.01351	0.003982215
CS	UT	С	0.01083	0.004059594
CS	SW	S	0.0064	0.003044667
CS	SW	Н	0.00265	0.003104642
CS	SW	С	0.00748	0.001407587
CS	75 G	S	0.00335	1.156231737
CS	75 G	Н	0.00443	0.00319813
CS	75 G	С	0.00208	0.002008515
CS	25 G	S	0.00708	0.001391294
CS	25 G	Н	0.0036	0.0005
CS	25 G	С	0.00994	0.001431328
U	Т	S	0.08918	0.021981035
U	Т	Н	0.023176667	0.033258536
U	Т	С	0.34205	0.22037107
U	UT	S	0.02575	0.005509374
U	UT	Н	0.05239	0.009630535
U	UT	С	0.0606	0.040254716
U	SW	S	0.138303333	0.004292742
U	SW	Н	0.06664	0.093084159
U	SW	С	0.460376667	0.035045833
U	75 G	S	0.09337	0.0033759
U	75 G	Н	0.0943	0.097564545
U	75 G	С	0.259973333	0.093947024
U	25 G	S	0.309295	0.416157824
U	25 G	Н	0.174866667	0.157631588
U	25 G	С	0.550693333	0.043379813

Table A-2. Average Mass Loss Data.



Material	Water:	Environment	Mass Loss (g/m^2*day) Average
CS	Т	S	4.161770029
CS	Т	Н	2.536637777
CS	Т	С	6.140558004
CS	UT	S	3.174481135
CS	UT	Н	4.265972162
CS	UT	С	6.839449077
CS	SW	S	4.041779694
CS	SW	Н	1.673549405
CS	SW	С	4.723830018
CS	75 G	S	2.115619059
CS	75 G	Н	2.797669382
CS	75 G	С	1.313578401
CS	25 G	S	4.471218787
CS	25 G	Н	2.273501078
CS	25 G	С	6.277389088
U	Т	S	0.92153
U	Т	Н	0.23949
U	Т	С	1.76726
U	UT	S	0.26608
U	UT	Н	0.54136
U	UT	С	0.3131
U	SW	S	1.42914
U	SW	Н	0.68861
U	SW	С	4.75724
U	75 G	S	0.96483
U	75 G	Н	0.97444
U	75 G	С	2.6864
U	25 G	S	3.19605
U	25 G	Н	1.80696
U	25 G	С	5.69051

Table A-3. Average mass-loss rate.



APPENDIX B. ANALYSIS OF TEST WATER

	Grey	water			Saltwate r	Treated wat	d Gray ter	25G	:75S	75G	:25S
Date	17-Feb	20-	26-	24-	17-Feb	17-Feb	26-	17-Feb	20-Feb	17-Feb	20-Feb
		Feb	Feb	Mar			Mar				
Sample ID	GW	GW	GW	GW	SW	GWT	GWT	25G:75	25G:75	75G:2	75G:2
Total Coliform (col/100 mL)	20050				42	20050	20050	s 20050	S	5S 2005	55
Fecal Coliform (col/100 mL)	20050				10	20050	20050	20050		2005	
Enterococci (col/100 mL)	12980				10	5600	100	6590		2005	
BOD5 (mg/L)	729	492	503	128	3	46	6	143	68		344
COD (mg/L)	1310		920		3	120	30	310		640	
Total Kjeldahl Nitrogen (mg/L)	8		6.6		170	0	2.12	2.7		5.3	
Nitrate-nitrogen (mg/L)	0.06		0		0.13	0.05	0.02	0.04		0	
nitrite-nitrogen (mg/L)	0.143		0.165		0.001	0.02	0.004	0.051		0.127	
ammonia-nitrogen (mg/L)	0.18		0.25		0.01	0.03	0	0.08		0.2	
total phosphorus as P (mg/L)	0.5		0.5		0.06	0.11	0.21	0.11		0.61	
total suspended solids (mg/L)	110		245		2	10	20	52		0.13	
alkalinity (mg/L)	51.5		68.6		203.8	62	13.3	168.4		94.2	
total iron (mg/L)	0.3		1.85		0.03	0.16	0.12	0.37		0.34	
total copper (mg/L)	0.71		2.71		0.06	0.3	0.15	0.58		0.7	
total manganese (mg/L)	0.05		0.21		0.06	0.02	0.03	0.08		0.06	
sulfate (mg/L)	49		48		2490	21	5	1931		705	
sulfide (mg/L)	6.4		2.13		0	0	0	0		1.9	
chloride (mg/L)	46		43		17793	11	18	13183		5250	
рН	5.5		5.7		7.99	6.97	5.86	6.98		6.24	

Table B-1. Analysis of test water at beginning of of mass loss (17 Feb) and electrochemical experiments (all other dates)



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APPENDIX C. MASS LOSS PHOTOGRAPHS (MICROSCOPE)

Water Type And Environment	Replicate 1	Replicate 2	Replicate 3
Treated Submerged			N/A
	Sample #2	Sample #3	Sample #
Treated Humid			
	Sample #4	Sample #5	Sample #6
Treated Cycled			
	Sample #7	Sample #8	Sample #9
Gray water Submerged	0	0	0
-	Sample #10	Sample #11	Sample #12
Gray water Humid	Complet #42	N/A	Completing of the second secon
	Sample #13	Sample #14	Sample #15

Table C-1. Photographs of coated/scribed sample coupons.



r			The second s
Gray water Cycled			0
	Sample #16	Sample #17	Sample #18
Seawater Submerged			
	Sample #50	Sample #20	Sample #21
Seawater Humid	0		6
	Sample #22	Sample #23	Sample #24
Seawater Cycled		0	0
	Sample #25	Sample #46	Sample #27
75 G Submerged			
	Sample #28	Sample #29	Sample #30
75 G Humid	Comple #24	Comple #20	N/A
	Sample #31	Sample #32	Sample #33

Table C-1. Photographs of coated/scribed sample coupons (continued).



75 G Cycled	.00		
	Sample #49	Sample #35	Sample #36
25 G Submerged	0		
	Sample #37	Sample #38	Sample #39
25 G Humid		0	
	Sample #40	Sample #41	Sample #47
25 G Cycled	(O)		TOO .
	Sample #43	Sample #44	Sample #45

Table C-1. Photographs of coated/scribed sample coupons (continued).



Water Type and Environment	Replicate 1	Replicate 2	Replicate 3
Treated Submerged			
	Sample #51	Sample #52	Sample #53
Treated Humid		24	
	Sample #54	Sample #55	Sample #56
Treated Cycled	Sample #57	Sample #58	Sample #59
Untreated	Sample #57	Sample #56	Sample #59
Submerged			
	Sample #60	Sample #61	Sample #62
Untreated Humid			
	Sample #63	Sample #64	Sample #65
Untreated Cycled	Sample #66	Sample #67	Sample #68

Table C-2. Photographs of uncoated sample coupons.



Water Type and Environment	Replicate 1	Replicate 2	Replicate 3
Seawater Submerged	1		
	Sample #69	Sample #70	Sample #71
Seawater Humid			
	Sample #72	Sample #73	Sample #74
Seawater Cycled			
	Sample #75	Sample #76	Sample #77
75 G Submerged			
	Sample #78	Sample #79	Sample #80
75 G Humid			
	Sample #81	Sample #82	Sample #83
75 G Cycled			
	Sample #84	Sample #85	Sample #86

Table C-2. Photographs of uncoated sample coupons (continued).



Acquisition Directorate Research & Development Center

Water Type and Environment	Replicate 1	Replicate 2	Replicate 3
25 G Submerged			
	Sample #87	Sample #88	Sample #89
25 G Humid			
	Sample #90	Sample #91	Sample #92
25 G Cycled			
	Sample #93	Sample #94	Sample #95

Table C-2. Photographs of uncoated sample coupons (continued).


APPENDIX D. MASS LOSS WHOLE SAMPLE PICTURES



Table D-1. Photographs of coated/scribed sample coupons.





Table D-1. Photographs of coated/scribed sample coupons (continued).





Table D-2. Photographs of uncoated sample coupons.





Table D-2. Photographs of uncoated sample coupons (continued).



APPENDIX E. ELECTROCHEMICAL EXPERIMENT TAFEL PLOTS

Mass Loss (g/m2/day)	Type of Water
6.2	25% gray water / 75% saltwater
11.4	75% gray water /25% saltwater
12.3	100% gray water
18.3	90% distilled water / 10% gray water
21.0	Saltwater

Table E-1. Electrochemical mass-loss results.



Figure E-1. Electrocorrosion Tafel plot, 25% gray water/75% seawater.





Figure E-2. Electrocorrosion Tafel plot, 75% gray water/25% seawater.



Figure E-3. Electrocorrosion Tafel plot; 100% gray water.





Figure E-4. Electrocorrosion Tafel plot; 10% gray water/90% distilled water.



Figure E-5. Electrocorrosion Tafel plot; 100% seawater



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APPENDIX F. SHIP CALCULATION SPREADSHEETS

0	Sum-1							fiew Ready	Normal V	
1 (Experimenta	Middle of Ocean	stics (Leaving)	Tank Characteri	s (Entering)	Characteristic	st. Trim / Tank	ermuda Op	►I Leaving B	Ā	
				-		-				61 62 63
The Draft at (m) 7,765	Inal Draft Sorward (m) 8:335	V(m) 0.3352	5IF (m) 0.3352	6Trim (m) -0.5704	MTC (MT-m/m)* 206.800	W = D from LCF (MT-m) -138644.4	Earling Draft aft (m) 8.1	Starting Draft forward (m)	1	55 Craft Difference
										25 25
	9056.1									2 2
	10743.7	102.1	8 65	107		63.1	107.7	107.7		52 18 C
	11704.4	297.0	39.4	297.0		123.4	297.0	297.0		52 14 P and 8
	-90 /4.4	327.5	-27.7	327.5	000	190.5	327.5	327.3		Spund 6 05
	-801.9	të i	-44.7	ster T	1	207.5	19.0	02.0		49 00
	0.00	0.0	-48 7 -47.4	8 3		210.2	0.00	207.2	50	47 7-8 Pan
	0.0	0.0	-86.7	0.0 /cilior ounder / com	Country And Do	249.5	0.0	216.2		46 5 Pand S
	W* D from I CF (MT-m)	anninn Mass /M TI	list from I CF (m)	Mass (Matrin Tons)	Density (kn/m3)	Dist from stern (m)	Unlime (m3)	Tank Canacity (m3)	l	44 44 TWW
	- ALCONOMIC - A									42
	1 5/ PSC	7 1126	1 84-	7 1126		201.0	1.82.00	1. 896		S DUE A C DP
	-25739.3	306.5	-84.0	306.5		246.8	307.8	307.8		39 5 0 5
	-25739.3	306.5	-84.0	306.5	1	246.8	307.8	307.8		38 5 CP
	-/3660.0	342.6	-09.1	342.5		231.9	344.1	344.1		37 0 02
	0.000002-	342.6	-09-1	242.6	995.7	20102 01102	U-655	344.1 0.022		and a second a
	-507-48-3	440.6	-115.2	440.6		278.0	442.5	442.5		24 3 Pand S
	-875/61.4	879.3	-99.6	879.3		262.4	883.1	883.1		33 4 Pand S
	61432.8	4483	137.0	448,3		25.8	450.2	450.2		32 21 P and 3
	W * D from LCF (MT-m)	I (MT)	JIST from LCF (m) Ful	Mass (Metric Tons) C	Density (kg/m3)	Dist from stern (m)	Volume (m3)	Tank Capacity (m3)	SINT:	M approved to the
										28
	E'CONT+									22
	4270.2	35.8	119.4	71.5		43.4	76.9	76.9	VFLW	25 HFO 20 C
	256-59.0	214.9	119.4	429.7		43.4	462.1	51812	ŝ	24 HFO 20 P
	4321.9	167.2	25.9	334.3		0.70	208.5	309.5		23 HFO 10 P
	1.0.4	1.66	20.0	10.55	000	121.0	70.5	20.5		
	81 29.5	259.9	31.3	519.8		131.5	559.0	559.0		20 HFO 13 S
	\$104.3	267.6	19.1	535.2		143.7	575.5	575.5	8	19 HFO 12 P
	-2207.4	0 251	-11.4	0.386		7/4.2	4151	415.1	6	
	W * D from LCF (MT-m)	anging Mass (MT)	Dist from LCF (m) Ch	Mass (Metric Tonis)	Density (kg/m3)	Dist from stem (m)	Volume (mD)	Tank Capacity (m3)		16 Fuel:
										13
	21370.63									11 12
	0.0	0.0	-151.0	0:0		014.0	0.0	700.2		10 Forpeak
	-504223.5	440.1	-113.8	443.1		276.6	430.6	430.6	1D 4 P&8	0 BW 2 3 A
	-268.25.9	121	.71.8	373.7		234.6	363.2	363.2	1	BW6 P&S
	44 19 5	660.6	-6.7	9 080	1029	169.5	642.0	642.0	Sad	7 BW 10-11
	1228-62.0	221.6	103.1	221.6		132 0	215.4	215.4	n u	A RW 13 PK
	165-40.6	742.4	22.1	747.4		140.7	726.3	726.3		4 BW 22 P8
	49900.7	340.6	140.5	340.0		10.0	0.100	301.2		3 Okeg
	W * D from LCF (MT-m)	anging Mass (MT)	Dist from LCF (m) Ch	Mass (Metric Tons)	Density (kg/m3)	Dist from stern (m)	Volume (m3)	Tank Capacity (m3)	Non:	2 BallastTa
-	_	H	6	-71	m	D	0	00	A	6

Table F-1. Vessel Trim Calculations – mid-ocean.



•	-0	Sum						Ready	al View	Norm	
Middle	an (Experimental)	ing) Middle of Oce	teristics (Leavi	Tank Charac	ristics (Entering)	Tank Characte	muda Opt. Trim	Leaving Ben	* *		
7.728	8.372	0.3723	0.3723	-0.7446	206,800	-153983.77	sorring bran an (m)	rait loiwaro/m/	0 Sarung	are outprener (m)	27 57
- P-A-EF					AND MAY - I - I						8 8
		-77024.0								,	54
		10743.7	1077	39,4	107.7		123.4	107.7		P and S	
		-3254.9	117.5	-27.7	117.5		190.5	117.5			51 90
		6.6906-	327.3	-27.7	327.3	1000	190.5	327.3		and S	16 05
		-2796.5	62.6	-44.7	62.6	1000	207.5	62.6			49 85
		-14077.9	297.2	-47.4	297.2		210.2	297.2		80	48 7-
		-51534.6	1057.6	-48.7	1057.6		211.5	1057.6		8 Pand 5	47 7-
		-18741.5	216.2	-86.7	216.2	Contraction of the second	249.5	216.2	A MARKED A	and S	46 SI
		W * D from ICF (MT-m)	100% Full (MT)	Dist from LCF(m)	Mass (Metric Tons)	Density (kg/m3)	Dist from stern (m)	13)	Volume	W	44 7
											43
											42
		-31554.1									41
		-4338.8	51.2	-84.7	341.7		247.5	343.1		and S	40 51
		-3860.9	46.0	-84.0	306.5		246.8	307.8			29 20
		-1960 g	46.0	-94.0	5 306		5 396	2076		61	22 22
		-2/UC-7	0.70	1.60-	2 676		0 166	0.700	T	e one o	00 00
		-3549.0	51.4	-69-1	342.6	995.7	231.9	344.1			35 60
		-/612.2	66.1	-115.2	440.6		0.872	442.5		o one v	1 14
		-13134.2	131.9	9.66-	879.3		262.4	1.688		and S	4
		9214.9	67.2	137.0	448.3		25.8	450.2		P and S	32 21
		4838.8	35.3	137.0	235.4		25.8	236.4		V 21 C	31 PV
		W * D from ICF (MT-m)	15% Full (MTI)	Dist from LCF(m)	Mass (Metric Tons)	Density (kg/m3)	Dist from stern (m)	п3)	Volume i	table Water:	30 Pa
											29
											28
											27
		7.0756	50.0	4,611	C.1.1		4,04	/0.3		O 20 OVIN	10 20
		40000	0.30	1101	2.70+		404	7.616		0.000000	2 2
		5 UE866	7.797	110.4	C.667		7.2V	5103		(113C) A ST 0	24
		0 1007	0.75	5.15	6.67		107.0	2020	T	O 13 B / STTD	22
		1440.2	35.7	25.9	111.4	OFF	137.0	8.611		O 13 P (SERV)	1
		8129.5	259.9	31.3	519.8		131.5	0.655		0 13 5	20 HF
		5104.3	267.6	19.1	\$35.2		143.7	\$75.5		O 12 P&S	19 HF
		-2207.4	193.0	-11.4	386.0		174.2	415.1		O 10 P&S	18 HF
		-7556.6	260.0	-29.1	520.0		191.9	1.655	and the second	C 9 P&S	17 HF
		W * D from ICF (MT-m)	S0% Full (MTI)	Dist from LCF(m)	Mass (Metric Tons)	Density (kg/m3)	Dist from stern (m)	13)	Volume	ē.	16 Fu
											5 5
											14
									T		12
		-88895.04									: 11
		-110265.7	726.5	-151.8	726.5		314.6	706.0		rpeak	10 Fo
		-50429.5	443.1	-113.8	443.1		276.5	430.6		V 2-3 AND 4 P&S	9 BV
		-26825.8	373.7	-71.8	373.7		234.6	363.2		V 6 P&S	88 84
		-4419.5	660.6	-6.7	660.6	5701	169.5	642.0		V 10-11 P&S	Z BV
		13732.2	458.9	29.9	458.9	4000	132.9	446.0		V 13 P&S	6 8V
		22862.0	221.6	103.1	221.6		50.7	215.4		V 18 P&5	vi S
		16540.6	747,4	22.1	747,4		140.7	726.3		~6 V 22 P&S	4 L
		W * D from UCF (MT-m)	100% Full (MT)	Dist from LCF(m)	Mass (Metric Tons)	Density (kg/m3)	Dist from stern (m)	13) (En	Volume	flast Tanks:	- L
								:			-
-		×	6	F	-	D	•			A	L

Table F-2. Vessel Trim Calculations – leaving Bermuda.



APPENDIX G. SHIP CALCULATIONS



Figure G-1a. Handwritten vessel operations, consumption, and production calculations.



16 APRIS Assuming: Fuel: Subtrat 2.3B m3/hr per set (20 \$ 9) This is TWW: Add 25 "In each to ypeak I skeg all empty Start: 8.659, 7.441 8.659, 7.441 & not what we want 1 hr: 8.662, 7.438 6 hrs 12 hr: 8.666, 7.434 Assume: Fuel: (2.38 "/hr por set (10312) TWW: (D 25 m3/m Mpech & skeg Stat: 8.472, 7.628 1 Wr : 8.473, 7.627 6 hr 8475, 7.625 12 hr: 8.477, 7.623 Fill Skig, put rest in TWW 120 hr: 600 m3 TWW, burn 28.56 fiel from each tank Fill Skee, put rest into 18C & 14 P35, take fuel from only 9 Stat: 9,472,7.628 12 hr: 8,309, 7.791 24 W: Distribute 600 - 3 to town tanks (Sharting From bottom up)

Figure G-1b. Handwritten vessel operations, consumption, and production calculations.

16 APR 15
Middle of Ocean
Fuel burn rate: 4.76 m3/hr (800 m3/7 day trip)
TWW Generation pate: 50 "/hr
Tanks Kept Full e all times: 2,3,4,6 P\$5, 10 P\$5, 11 P35 (1436 m3)
Tanks to Fill w/ Tww : Forepeak & Skeg
Forepeak: 70% = 3, 726.5 MT
Skeg: 331.0 m", SHO.C MT
Fill Foreback & skeg: 2-300 m3 in 4peak for quick adjustment Typically empty in transit What Is get as close to 8 \$ 8.1 is possible Assume burning 20P30 \$ 9P\$5
<u>Hr. 1</u>
BB Subtract 1.19 m2 from each (2.38 From each set)
Add 25 "The to Forepeak & skey (Assuming all Thomas generated goes to ballast tanks)
Before: 8.659,7.441
After: 8.659,7.441
After 6 hrs
Sublet 5 x 2.28 = 11.9 to each
Add 5×25=125 to each
Before: 8.659,7.441 After: 8.662,7.438

Figure G-1c. Handwritten vessel operations, consumption, and production calculations.

Spreadsheets Entering Bermude: Based on loading given to us, change in trim was calculated based on the optimum trim (8.1 m by stern, 8.0 by ba) 1 same for kenning Bermuda Middle of Ocean: use spreadsheet to look at hour by hour change in trim, based on fuel burn rate & treated wastewater generation rate. More things around in tanks to see if the trim can be maintained. * Superimpose hull view onto block drawing # 2 .- x .-* Middle of ocen, change 4-peck & skey * * Balance Fresh & westewater production * * Photos & graphics Pic Takeway: Type of water is most important, Not necessorily taule condition

Figure G-1d. Handwritten vessel operations, consumption, and production calculations.



Figure G-1e. Handwritten vessel operations, consumption, and production calculations.



OGHPRIS
PILLING INTO BERMUDA, OPTIMUM TRIM
1) ASSUME LCF is a AMIDSHIPS (162.81 m) 2) ASSUME LCF to FP \$ AP = $\frac{1}{2}$ LBP -> LBP= 300.12 m
$MTC = 2068 \frac{tm}{cm} \cdot \frac{100 cm}{1m} = 206,800 \frac{tm}{m} \frac{mdm lon-mder}{meter}$
STRIM = WADFOR LCP
FUELS MT1
HFO 9 P\$5: (-(260.001 m7)(29.064 -)) = -7556.643 MT-m
HFO 10 P35: (-(153.0215 MT)(11.436 m)) = -2207.354 MT - m
HFO 12 P\$ 5 : (267.6075 MT (19.074 m)) = 5104.345 MT-M
14F0 13 5 : (259.91175 mr (31.273 m))= 8129.520 mr-m
HFO 13 P : (55.707 MT (25.854 -))= 1440.249 MF.
HFU 13 OVELOW: (36,9675 MT (31,273 m)= 1152,269 MT-M
HPO 13 P JETT: (167.1675 MT (25.854 m))= 4321.949 MT-m
HED 20 P # 5: (241.428 MT(114.419 m))= 28830.849 Mr-m
HED 20 OVELOW: (35.7585 MT (119.418 m))= 4270.209 MT-M
434 89.353 MT-M
STMN = <u>43484.353 MT-M</u> = 0.2103 M
POTABLES
PROM SPRENDSHEET:
$S_{\text{TRim}} = \frac{-210360.633 \text{ MT-m}}{206900 \text{ MT-m}} = -1.017 \text{ m}$
0.2103-1.017 = - 0.8067 m
0.8067 m by bow





STF = 150.06 m (0.9067) = 0.40335 m
$S_{TA} = \frac{150.00m}{300.12m} (0.9007) = 0.40335m$
STF = 8.0 ~ + 0.40335 ~ = 8.40335 ~
STA = 8.1 m - 0.40335 m = 7.69665 m

Figure G-1g. Handwritten vessel operations, consumption, and production calculations.





Figure G-1h. Handwritten vessel operations, consumption, and production calculations.



$$\begin{split} \delta_{TF} &= \frac{50.06m}{200.12} (1.118m) = 0.579 m & Pacing LCF TO FP \\ &= \frac{1}{2} LBP \\ \delta_{TA} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} (1.193-) = 0.599 m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} m \\ \\ \delta_{TP} &= \frac{150.0c}{200.12} m \\ \\ \delta_{TP} &= \frac{10.0c}{200.12} m \\ \\ \delta_{T$$

Figure G-1i. Handwritten vessel operations, consumption, and production calculations.





Figure G-1j. Handwritten vessel operations, consumption, and production calculations.



APPENDIX H. SHIP TANK CAPACITY DIAGRAMS



Figure H-1. Treated waste water tanks.





Figure H-2. Potable water tanks.





Figure H-3. Fuel tanks.





Figure H-4. Ballast tanks.

