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Investigation Of Ballast Water Treatment's Effect On Corrosion

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Investigation Of Ballast Water Treatment's Effect On Corrosion

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16. Abstract (MAXIMUM 200 WORDS) The objective of this study was to characterize the corrosion behavior associated with ballast water treatments on ballast tank and piping alloys common to oceangoing and fresh water vessels. The work compares and contrasts the effect of ballast water treatment methods on various alloys routinely encountered in ballast tanks and ballast water systems aboard both fresh water and ocean going vessels. Controlled laboratory tests were conducted using simulated chlorination, deoxygenation and chlorine dioxide disinfection. Materials were exposed to three environments: the humid or overhead environment, alternate immersion, and constant immersion. The tests were divided into two phases: the Seawater Phase and the Freshwater (Great Lakes Water) Phase and was based on guidance provided by the International Maritime Organization. Natural, unfiltered seawater obtained from Key West, FL, for seawater testing; Great Lakes water was supplied by collecting water from Lake Superior at the Arthur McClure Marine Terminal in Duluth, MN. The set up and test procedures of both the Seawater Phase and the Great Lakes Water Phase were identical, in as far as is practicable.					
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EXECUTIVE SUMMARY

The movement of non-indigenous species via ballast water and their introduction into coastal waters by way of ballast water is an ongoing problem, both domestically and internationally. Ballast water discharged from ships is one of the vectors aquatic nuisance species (ANS) have been introduced. In response to the concerns from ANS, the National Invasive Species Act of 1996 (NISA) was adopted. To comply with the management guidelines in NISA, the United States Coast Guard (USCG) has established both regulations and guidelines to prevent the introduction of ANS.

In response to these regulations and guidelines, several Ballast Water Management Systems (BWMS) have been developed to treat ballast water. Most of the technologies have been developed by vendors, which have their basis in land-based applications for industrial and municipal water treatment. To date, the chief effort on studies of BWMSs has been on the treatment system efficacy and effects on organisms prior to discharge. One of the risks of treating ballast water is the potential to increase the rate of corrosion in the ballast tanks and piping system, which can affect the ships' safety and normal maintenance procedures. For the maritime industry, corrosion and corrosion protection is a considerable cost in the normal operation of a vessel. As a consequence, any BWMS that increases corrosion rates may not be used even if the ballast water treatment performance is satisfactory. As such, the USCG needs to understand how use of BWMSs affects the corrosion rates of ballast tanks and piping systems.

Currently, there is little background information on BWMSs and their effects on materials and coatings exposed to treated ballast water. The Naval Research Laboratory in Key West, FL has been funded through a Military Interdepartmental Purchase Request (MIPR) by the United States Coast Guard (MIPR HSCG32-11-X-R00005) to investigate the corrosion effects caused by ballast water management systems over a period of six months.

The current work compares and contrasts the effect of ballast water treatment methods on various alloys routinely encountered in ballast tanks and ballast water systems aboard both fresh water and ocean going vessels. Treatments included deoxygenation, chlorination and chlorine dioxide treatment. Materials were exposed to three environments: the humid or overhead environment, alternate immersion, and constant immersion. The test was divided into two phases: the Seawater Phase and the Freshwater (Great Lakes Water) Phase. The set up and test procedures of both the Seawater Phase and the Great Lakes Water Phase were identical in as far as is practicable.

The results for exposure in seawater environments, described herein, indicate that corrosion rates in the humid environment generally increased above treated seawater, relative to untreated seawater, regardless of treatment. In the alternate immersion environment, deoxygenation resulted in increased rates on steel and brass and decreased rates on copper-nickel. Chlorination and chlorine dioxide treatment improved or had a negligible effect on the corrosion rate of all metallic materials tested. Deoxygenation improved the performance of uncoated steel and copper-nickel in a constantly immersed seawater environment, but generated increased rates on scribed specimens and brass. Chlorination and chlorine dioxide treatment in the constant immersion environment reduced or had negligible effect on corrosion rates.

With respect to Great Lakes water, deoxygenation generally showed a decreased effect or a negligible effect on corrosion rates of all materials, as compared to the untreated lake water. The exceptions were cast iron in the humid environment and cathodically protected steel in alternate immersion. In the humid environment, chlorination resulted in equal or improved corrosion rates on all materials except uncoated

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steel. Alternate and constant immersion results were mixed in chlorinated lake water. Corrosion rates increased in the chlorinated alternate immersion environment for brass, copper-nickel and uncoated steel. The corrosion rates for cast iron and cathodically protected steel decreased in the same environment. In constant immersion, chlorination resulted in increased rates for cast iron and copper alloy, while remaining virtually unchanged for cathodically protected and uncoated steel. Chlorine dioxide treatment resulted in increased corrosion rates on all materials in the humid environment. In the alternate immersion environment, cast iron and cathodically protected steel specimens experienced reduced corrosion rates as compared to untreated lake water, while the remaining materials experienced increases. In the constant immersion environment, only cast iron experienced a corrosion rate decrease.



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LIST OF ACRONYMS, ABBREVIATIONS, AND SYMBOLS

ANS	Aquatic Nuisance Species
ASTM	American Society for Testing and Materials
BWMS	Ballast Water Management Systems
C	carbon
cm	centimeter
CP	cathodic protection
Cr	chromium
Cu	copper
DO	dissolved oxygen
DPD	N,N-diethyl-p- phenylenediamine
Fe	iron
IMO	International Maritime Organization
L	liter
MEPC	Marine Environment Protection Committee
mg	milligram
MIPR	Military Interdepartmental Purchase Request
mL	milliliter
Mn	manganese
Mo	molybdenum
mpy	mils per year
Ni	nickel
NISA	National Invasive Species Act
NRLKW	Naval Research Laboratory Key West
NSW	natural seawater
P	phosphorous
Pb	lead
PE	polyethylene
ppm	parts per million
PTFE	Polytetrafluoroethylene
PVC	polyvinyl chloride
S	sulfur
Si	silicon
Sn	tin
TRO	Total Residual Oxidant
USCG	United States Coast Guard
VOC	Volatile Organic Compound
Zn	zinc



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1 INTRODUCTION

Corrosion is a common problem on vessels that impacts ship owners from both economic and operational aspects. The Naval Research Laboratory Key West (NRLKW) has been tasked with researching how different ballast water treatment systems affect corrosion rates for materials common to ballast tank systems. Previously, a scoping study was completed through a literature review to assess the corrosion behavior of shipboard materials normally exposed to ballast water, assess how different ballast water treatment processes may affect the corrosion rates of these materials, and how regulators would assess corrosion acceptability as part of ballast water treatment system type approval.

NRLKW conducted corrosion related experiments to characterize corrosion behavior caused by ballast water treatment technologies. The test was divided into two phases: Seawater Phase and Great Lakes (or fresh) Water Phase and was based on guidance provided in the Marine Environment Protection Committee (MEPC) Report 59/2/16ⁱ, published by the International Maritime Organization (IMO). The set up and test procedure of both the Seawater Phase and the Great Lakes Water Phase was identical in as far as is practicable.

The objective of the seawater phase was to characterize the corrosion behavior associated with ballast water treatments on ballast tank and piping alloys common to oceangoing vessels, while the Great Lakes water phase was aimed at the characterization of the corrosion behavior associated with ballast tank and piping alloys typical of fresh water vessels. The treatments that were applied to natural seawater and Great Lakes water simulated chlorination, deoxygenation, and chlorine dioxide disinfection. All testing was conducted at NRLKW. Natural, unfiltered seawater was supplied for seawater testing; Great Lakes water was supplied by collecting water from Lake Superior at the Arthur McClure Marine Terminal in Duluth, MN and shipping it to Key West.

Three replicates of each specimen type were installed at three different heights in the exposure trough. Over a total period of 180 days, exposure troughs simulated ballast operations by filling and holding the water in the trough for one week, then partially draining and holding for a period of one week such that the lower specimens experienced constant immersion, the middle row experienced alternate immersion and the top row experienced high humidity with no immersion. Specimens were visually evaluated monthly and again at the end of testing for corrosion damage. Weight or mass loss analysis was performed to quantify corrosion rates. Constant immersion testing and weight loss analysis were performed in accordance with American Society for Testing and Materials (ASTM) Standard G31-72 (2004)ⁱⁱ and alternate immersion was based on ASTM G44-99 (2005)ⁱⁱⁱ.

2 TEST MATRIX

Table 1 and Table 2 provide the test matrices for the seawater and Great Lakes water phases, respectively. With regard to the seawater phase, seven types of specimens were exposed to untreated seawater and the three variations of treated seawater. Ballast and holding tanks are generally fabricated from either uncoated or coated carbon steels. Coated carbon steel specimens with scribes served to simulate coating damage. The scribed specimens with cathodic protection (CP) were included since seawater ballast tanks are typically cathodically protected for corrosion control. Copper-nickel and brass alloys are common materials for piping and fittings. Cast iron is often used for valve bodies in non-seawater applications, therefore cast iron was not tested under seawater conditions. Coated specimens were excluded from the Great Lakes water phase given that ballast tanks in fresh water vessels are typically not coated. Typical compositions of the metallic components of the test matrix are presented in Table 3.



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Table 1. Seawater phase test matrix.

Material	Condition	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Uncoated Carbon Steel (AISI 1020)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Coated Carbon Steel	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Coated Carbon Steel with Scribe	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Coated Carbon Steel with Scribe, Cathodically Protected	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Brass (CDA464)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Copper-Nickel (CDA706)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
PTFE with Silica Fibers (Garlock GYLON® 3500)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Specimens per Trough		63	63	63	63

Table 2. Great Lakes water phase test matrix.

Material	Condition	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Uncoated Carbon Steel (AISI 1020)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Cast Iron	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Uncoated Carbon Steel, Cathodically Protected	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Brass (CDA464)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Copper-Nickel (CDA706)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
PTFE with Silica Fibers (Garlock GYLON® 3500)	Humid Environment	3	3	3	3
	Alternate Immersion	3	3	3	3
	Constant Immersion	3	3	3	3
Specimens per Trough		54	54	54	54

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Table 3. Composition of alloys in the test matrix, all values are in weight percent.

	Fe	C	Cr	Cu	Mn	Mo	Ni	P	Si	S
Cast Iron	Bal.	3.25-3.50	0.050-0.450	0.15-0.40	0.50-0.90	0.050-0.100	0.050-0.200	<=0.12	1.80-2.30	<=0.15
Carbon Steel	99.08-99.53	0.17-0.23			0.30-0.60			<=0.040		<=0.050
	Fe			Cu	Mn	Sn	Ni	Pb	Zn	Other
Brass	<=0.10			59.0-62.0		0.50-1.0		<=0.20	39.25	
Copper Nickel	1.00-1.80			88.7	<=1.0		9.0-11.0	<=0.050	<=1.0	<=0.50

3 EXPERIMENTAL SET UP

3.1 Specimen Preparation

All specimens in the test matrix measured 2-inches x 3-inches x 1/8-inches with the exception of the cast iron. Cast iron specimens were 1/4-inch thick, as this was the minimum available thickness. All steel and cast iron specimens were grit blasted with aluminum oxide grit, followed by a degreasing procedure (wash with methanol or acetone). Brass and copper-nickel specimens were degreased. Following degreasing, all specimens were weighed with a Sartorius Genius scale with a resolution of 0.1 milligram (mg) and weights were recorded. With regard to the uncoated steel and cast iron specimens, this procedure was carried out as close to deployment as possible to minimize flash rust on the specimens. The Garlock Glyon® gasket material required no surface preparation other than a solvent wash. Following the wash, the gasket material specimens were weighed to the nearest 0.1 mg. All specimens were photographed, front and back, and were assigned a unique identifier.

Cathodically protected steel specimens for the Great Lakes water phase were not coated. A hole was drilled in the approximate center of the specimen, as shown on the left in Figure 1. The holes were de-burred and large enough to accommodate a 10-24 screw. These specimens were then grit blasted, degreased and weighed to the nearest 0.1 mg. Following weighing, a 1-7/8-inch diameter rudder zinc was attached as shown on the right. The lead wire from the anode was for the purpose of measuring potential.

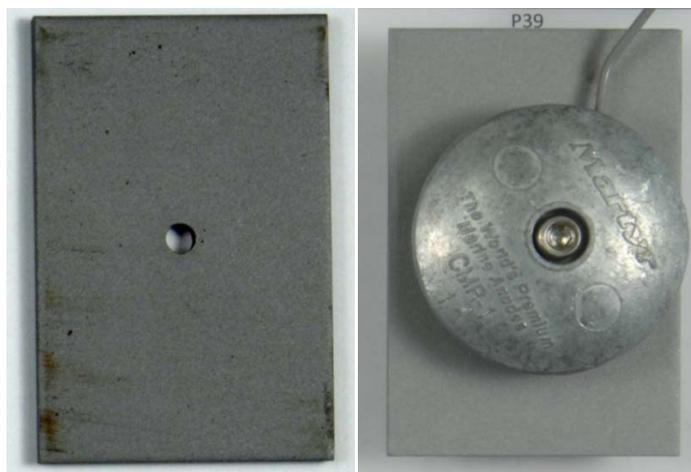


Figure 1. Cathodically protected specimen for Great Lakes water exposure.



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The coated and cathodically protected specimens for exposure in seawater were prepared by drilling a hole approximately 1/4-inch from the top of the specimen, as shown in Figure 2. The holes were centered, deburred and large enough to accommodate an 8-32 screw. These specimens were then grit blasted, degreased and weighed in the same manner as the steel specimens discussed above. Following initial weighing, wiring for connection to the anode was attached.



Figure 2. Electrical connection to anode prior to coating.

Following wire attachment, the cathodically protected carbon steel specimens to be exposed to seawater were coated with two coats of Intershield 300V, as manufactured by International Coatings. The “V” version of this coating is the volatile organic compound (VOC) compliant version available in the U.S. The coating was applied by brush, according to the manufacturer’s recommendations. Following application and curing of the coating, the cathodically protected specimens were scribed then weighed a final time and the weights recorded. A coated and scribed specimen, ready for deployment under cathodic protection is shown in Figure 3. A 2-13/16-inch rudder zinc was used for each set of nine seawater exposure specimens in the cathodically protected condition.



Figure 3. Coated and scribed specimen.



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Coated and scribed, but not cathodically protected specimens were prepared in a manner similar to the coated, scribed and cathodically protected specimens but without the electrical connection. These were grit blasted, degreased, and weighed in a manner similar to the coated, scribed and cathodically protected specimens, with weights taken prior to and following coating and scribing. Scribed specimens, with or without cathodic protection, were scribed in accordance with ASTM D1654-92 (2000)^{iv} as shown in Figure 4.



Figure 4. Scribed specimen.

3.2 Specimen Support

All specimens were supported on racks fabricated from perforated polyvinyl chloride (PVC) sheet and threaded nylon standoffs. Three or four standoffs per specimen were threaded into the perforations in the PVC sheet such that two standoffs supported the specimen from below and the remaining standoff(s) stabilized the specimen from above. A representative photograph is shown in Figure 5. Three specimens were mounted at each of the three levels. The lowest specimens were wetted at all times for the duration of the test. The middle level of specimens were subjected to alternate exposure cycles of seven days wet, seven days dry. The uppermost specimens were not wetted, but exposed to the humid atmosphere of the overhead space.

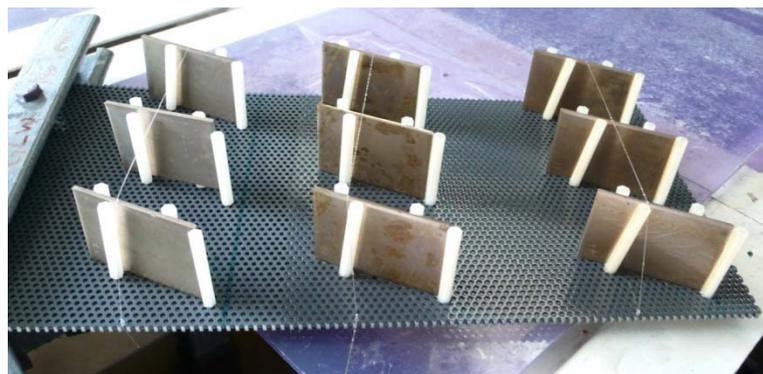


Figure 5. Specimen rack.

The perforated PVC sheets supporting the specimens were through-bolted to a length of fiberglass channel strut, a schematic of which is provided in Figure 6. This facilitated removal of each specimen set for inspection and photographic documentation. A frame, constructed of channel strut, shown in Figure 7 was placed inside the trough to support the specimen racks, below the trough flange, allowing the entire



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assembly to hang freely below the level of the lip of the trough. In order to minimize exchange with air outside the trough and maintain a humid environment, each trough was covered with a clear PVC sheet. A diagram of the cross section of the exposure trough showing a deployed support rack is given in **Error! Reference source not found.**

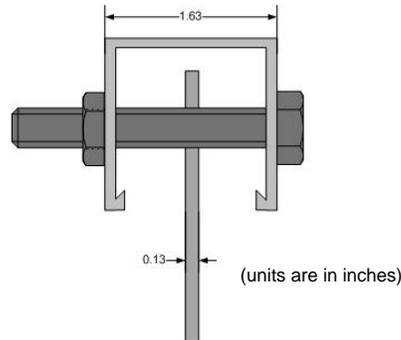


Figure 6. Schematic of through-bolting of PVC sheet to channel strut.

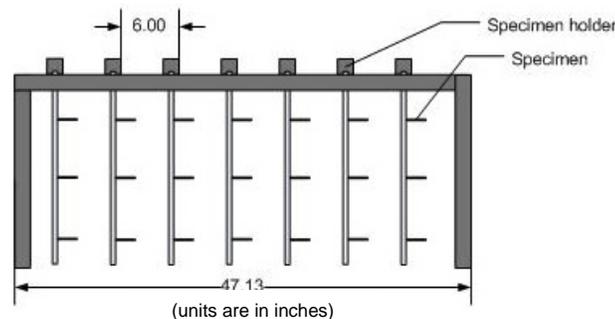


Figure 7. Specimen support rack.

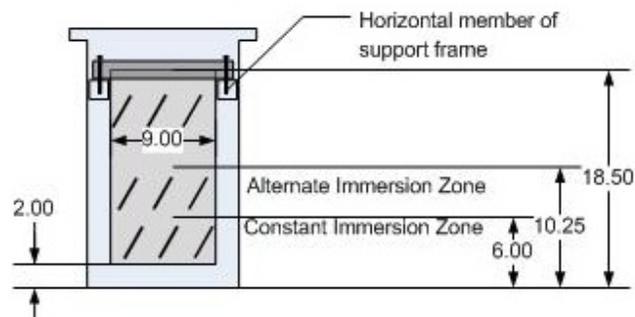


Figure 8. Cross section of exposure trough showing submerged support rack.

3.3 Trough Configuration and Specimen Exposure

Testing utilized eight fiberglass exposure troughs. The interior dimensions of each exposure trough measured 96-inches in length, 12-3/4-inches in width and 22-inches in depth. Each seawater trough was filled from a common source and was connected to a common drain. The height of the fluid in each trough was controlled by the height of the standpipe inserted into the trough drain. The standpipe was made of two sections. For constant immersion testing, the standpipe height allowed the fluid to remain at a level sufficient to provide constant immersion of the lowest specimens. An extension to that standpipe was

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manually added to allow increased water level height for the wetted portion of alternate immersion exposure and was subsequently removed for the dry portion of alternate immersion exposure.

Lake water troughs were filled by pumping water from the Lake Superior shipping container directly to the untreated trough or a 40-gallon polyethylene (PE) tank (treatment tank) mounted in each trough requiring treatment. The common drain on the lake water troughs was capped to prevent accidental discharge. Discharge was achieved by pumping the lake water to a drain leading to the laboratory's sanitary sewer and subsequently the sewage treatment plant.

In order to facilitate water treatment and subsequent transfer of the treated fluid, each treatment tank was fitted with a commercially available 12-volt bilge pump to facilitate transfer of the fluid from the tank to the exposure trough. The pump outlets were routed through the wall of the tank with the outlet below the constant immersion water line, preventing unnecessary aeration of the transferred fluid. A plan view and profile view of the exposure trough layouts for treated troughs are given in Figure 9. All specimens were deployed prior to initial introduction of fluid into the exposure trough.

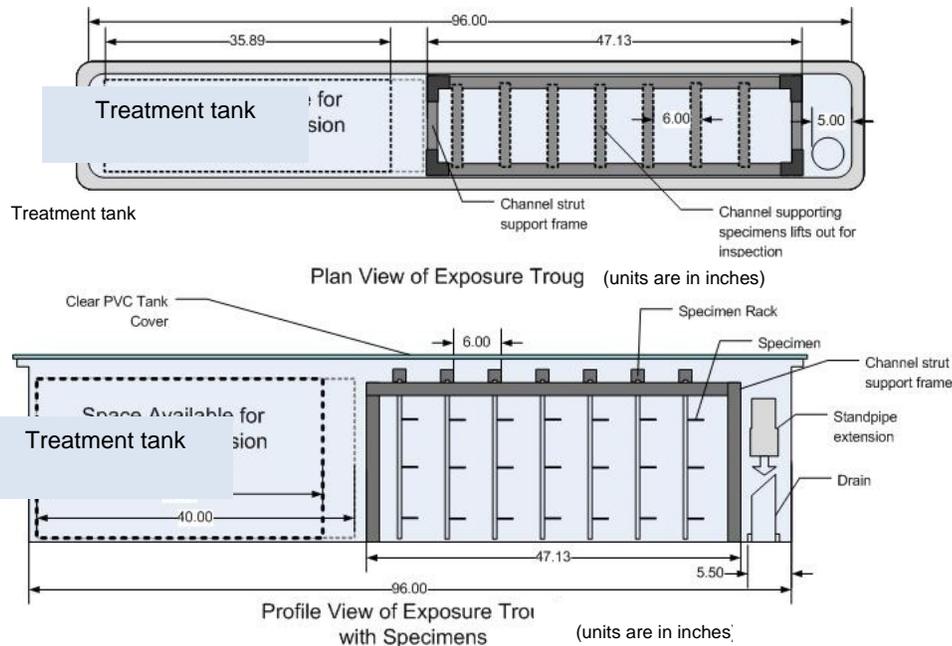


Figure 9. Plan and profile of exposure trough.

Great Lakes water exposure troughs had six specimen racks deployed in the trough at evenly spaced intervals, while seawater exposure troughs had seven sets of specimens. The wires from the cathodically protected specimens were terminated at a terminal block mounted above the waterline. A typical exposure trough is shown on the left in Figure 10; the array of eight exposure troughs is shown on the right.

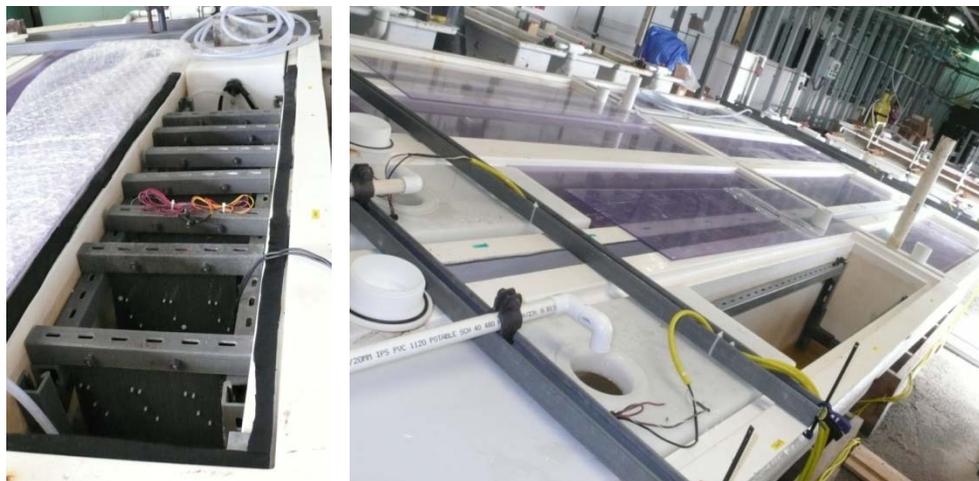


Figure 10. Exposure troughs.

3.4 Treatment Methods

Experimental testing required treatment, addition of, monitoring, and discharging of eight test fluids:

- Untreated seawater
- Deoxygenated seawater
- Chlorinated seawater
- Chlorine Dioxide treated seawater
- Untreated Great Lakes water
- Deoxygenated Great Lakes water
- Chlorinated Great Lakes water
- Chlorine Dioxide treated Great Lakes water

The basic approach for treatment of seawater and Great Lakes water was identical for each of the three treatment methods tested. The approach used to achieve each treatment method, including untreated, monitoring procedures and discharge considerations are detailed below. Water parameters were measured using a Hach HQ40d Multi Parameter meter prior to and following each alternate immersion fill and alternate immersion drain. Dissolved oxygen (DO) was measured with a Hach LDO101 IntelliCAL Standard Dissolved Oxygen Probe. The Hach HQ40d is also capable of measuring pH, with an IntelliCAL PCH101 pH electrode and conductivity with an IntelliCAL CDC 401 conductivity probe. Temperature is also available with any of the probes used.

3.4.1 Untreated Water

Untreated seawater or untreated Great Lakes water was introduced directly into the trough from the respective supplies. No treatment tank was required. Once specimens were immersed, flow of water was stopped; this was not a continuous refresh scenario. The respective water levels for the alternate immersion specimens were raised by adding water to the level of a standpipe extension and lowered by draining following removal of that extension.

Discharge Treatment

No treatment was necessary for seawater. Lake water was discharged to the sanitary sewer.



3.4.2 Deoxygenated Water

NRLKW achieved deoxygenation by purging water in the treatment tank with nitrogen to obtain an initial oxygen concentration of 0.2 mg/L. During transfer, the overhead space in the exposure troughs, each of which have a volume of approximately six cubic feet, was filled with nitrogen through continued purging of the fluid to minimize re-absorption of oxygen during transfer. The deoxygenation troughs were covered with clear PVC sheet to minimize the reintroduction of oxygen. Although neoprene gasket material was used to seal the space between the trough flange and the PVC sheet, the trough was not expected to remain completely airtight. Some re-absorption would likely occur. Troughs were sparged daily to reduce reabsorbed oxygen levels to below 1.0 mg/L.

Discharge Treatment

No treatment was necessary for seawater. Lake water was discharged to the sanitary sewer.

3.4.3 Chlorinated Water

Commercially available chlorine bleach is a common source of sodium hypochlorite, the active ingredient in the chlorination procedure. Clorox[®] bleach, which has an available sodium hypochlorite concentration of approximately 5.7%, was used as the source of sodium hypochlorite. When chlorine is added to water, some of the chlorine reacts first with organic materials and metals in the water and is not available for disinfection (this is called the *chlorine demand* of the water). The remaining chlorine concentration after the chlorine demand is accounted for is called *total chlorine*. Total chlorine is further divided into: 1) the amount of chlorine that has reacted with nitrates and is unavailable for disinfection which is called *combined chlorine* and, 2) the *free chlorine*, which is the chlorine available to inactivate organisms.

The total chlorine demand of both seawater and lake water can vary with location, temperature and time of year. In seawater, the addition of sodium hypochlorite to seawater results in the formation of hypochlorous and hypobromous acids as well as hypochlorite and hypobromite. The chlorine demand was determined by treating the seawater with known aliquots of chlorine containing solution (Clorox[®]) and measuring the residual concentrations following a chosen period – in this case, one hour. The demand is the difference between the initial concentration and the final concentration. This is in accordance with the set up procedure contained in ASTM D1291-01^v. However, ASTM D1291-01 follows with a wet chemistry titration. NRLKW has estimated the chlorine demand of the local seawater to be approximately 1.0 mg/L. Chlorine demand of the lake water varied during testing and ranged from 2.0 mg/L to 35.2 mg/L. Chlorine measurements were made with a Hach Chlorine Colorimeter II Test Kit. This kit has a range of 0.00 to 8.8 mg/L, which necessitated dilution of the treated water to verify the target 10 mg/L concentration, thus introducing a level of error. Using these values in conjunction with the information provided on the Clorox[®] label, it was determined that a volume of 29.2 mL of standard strength Clorox[®] bleach was required to treat 35 gallons of seawater. Due to the fluctuation of chlorine demand in lake water, the volume of standard strength Clorox[®] bleach required ranged between 37.1 mL and 94.0 mL.

The respective type of water was added to the treatment tank, where it was treated with the chlorine containing solution. Dosage was based on providing a 10 mg/L (or slightly higher) total residual oxidant (TRO) in the treatment tank. The water from the treatment tank was then transferred to the exposure trough, where chlorine concentrations were measured to verify residual levels. The chlorinated troughs were covered with PVC sheets to prevent degradation of the chlorine due to sunlight.

Discharge Treatment

All chlorinated waters were discharged into sanitary sewers.

3.4.4 Chlorine Dioxide Treatment

Due to the complexities and concerns in handling chlorine dioxide gas, a viable alternative, in a concentrated liquid form was identified. CDG Solution 3000, manufactured by CDG Environmental, Bethlehem, PA was used to prepare a solution with a 5 mg/L residual prior to introduction to the specimens. CDG Solution 3000 is a ready to use aqueous chlorine dioxide solution, available in one liter bottles, with a chlorine dioxide concentration reported to be 3000 mg/L. Prior to the start of the test, NRLKW conducted tests similar to the chlorine demand tests described above, to determine CDG Solution 3000 concentrations required for the desired residual. Chlorine dioxide concentrations were measured with a Hach Chlorine Dioxide Pocket Colorimeter II Test Kit, with a range of 0.05 to 5.0 mg/L, therefore the solution required dilution prior to testing. The troughs treated with chlorine dioxide were covered, but were not expected to remain airtight.

Discharge Treatment

It was expected that at the end of the weekly cycle the chlorine dioxide will have been degraded or consumed in the trough to a point where it is no longer measurable. Chlorine dioxide degrades rapidly in sunlight or with agitation. NRLKW ascertained that the residual chlorine dioxide levels were below 1.0 mg/L prior to discharge, however, the effluent was still discharged to a sanitary sewer system for both seawater and lake water.

3.5 Post Exposure

Following exposure, all specimens were photographed in the “as removed” condition. They were then cleaned in accordance with ASTM G1-03 (2011)^{vi}, which included mechanical abrading and rinsing with an organic solvent. Following cleaning, the specimens were weighed, final mass loss calculated and final post-cleaning photographs taken.

4 RESULTS AND DISCUSSION

4.1 Seawater and Great Lakes Water Properties – Untreated

Seawater used for this work was natural, unfiltered seawater pumped from the waters surrounding Key West, Florida. The pH of the seawater feed ranged from 7.90 to 8.08, resistivity ranged from 16.1 ohm-cm to 18.6 ohm-cm, dissolved oxygen varied between 6.50 and 9.72 mg/L and temperature ranged from 75.6 to 87.8 degrees F. The data plotted on a fill week basis for the duration of the test is shown in Figure 11.

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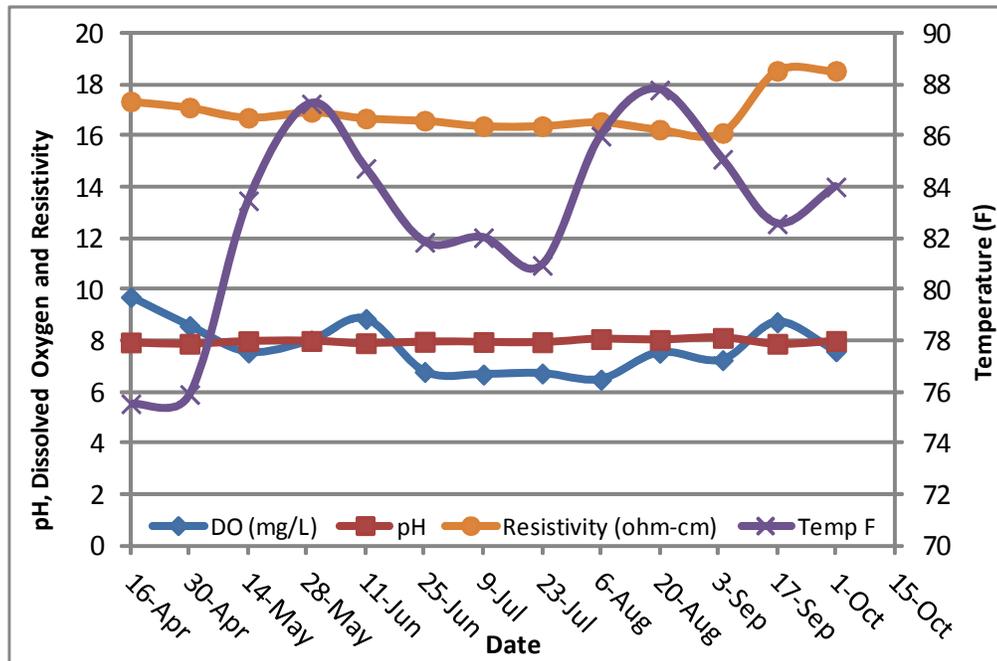


Figure 11. Properties of untreated seawater.

The Great Lakes water was collected from Lake Superior in Duluth, Minnesota. Water properties were recorded at the time of collection and are shown in Figure 12. Lake water properties recorded upon arrival in Key West are given in Figure 13. The resistivity of the Great Lakes water as collected ranged from 5,170 ohm-cm to 10,000 ohm-cm. Resistivity values measured in Key West ranged from 4,606 ohm-cm to 8,299 ohm-cm.

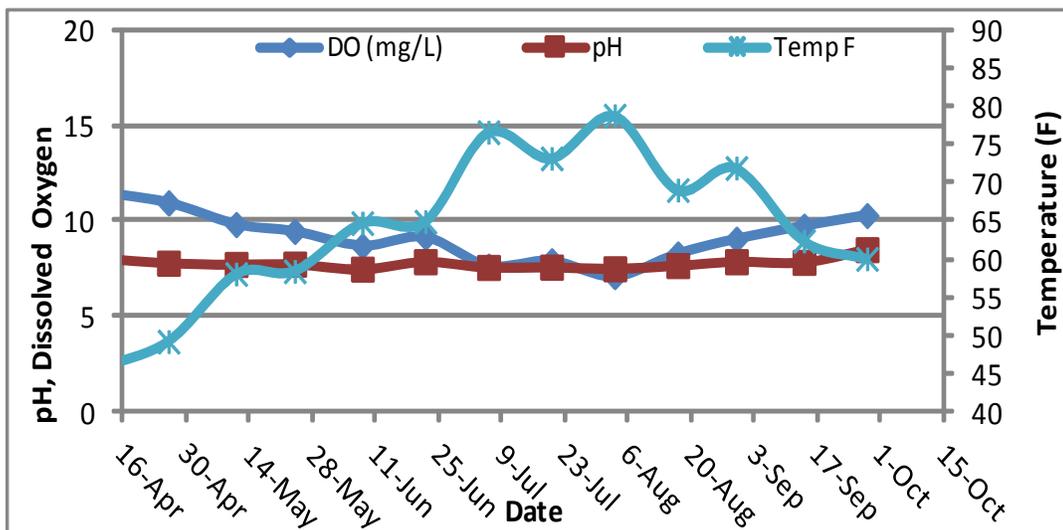


Figure 12. Properties of Great Lakes water, as collected in Duluth, Minnesota.



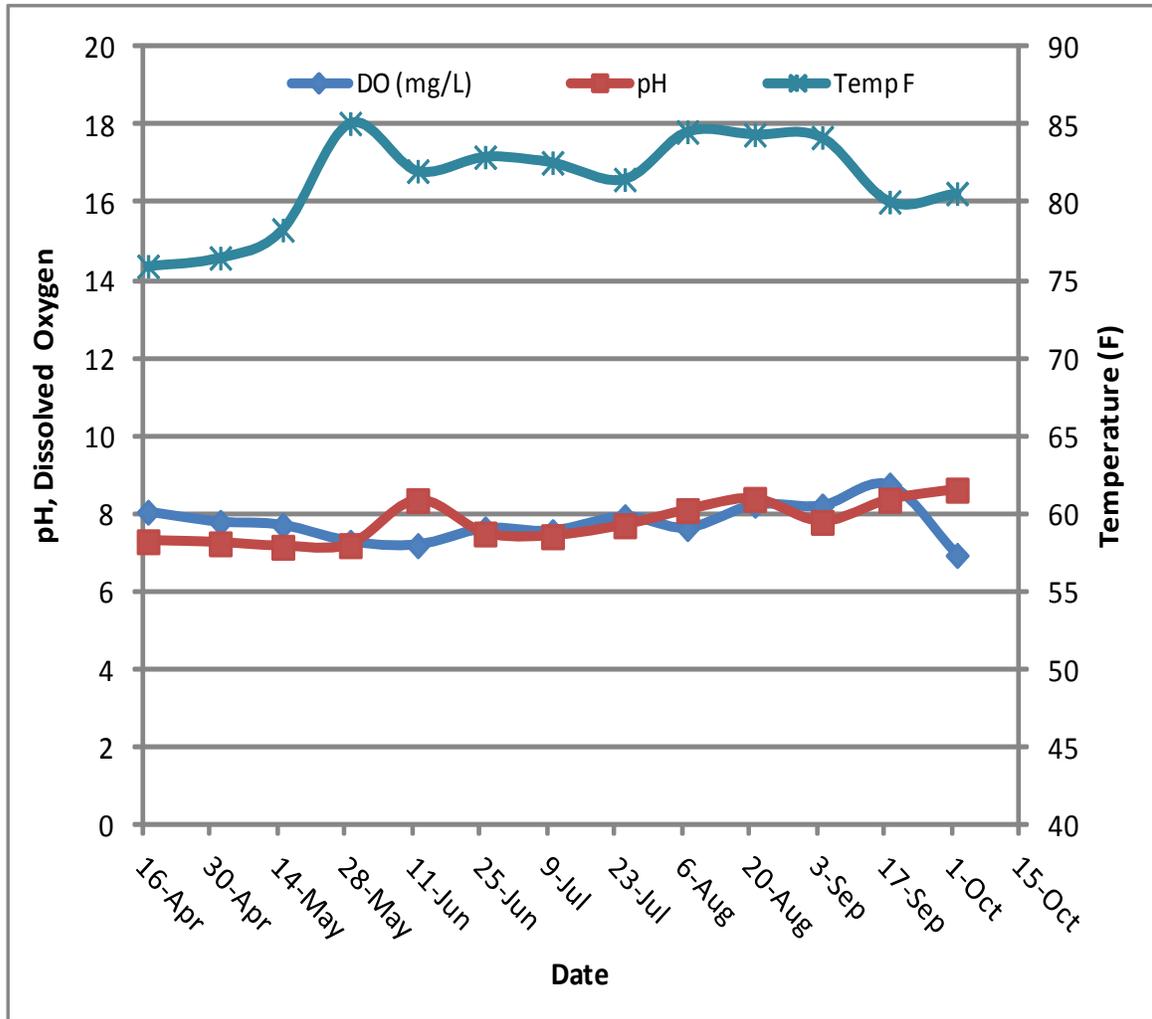


Figure 13. Properties of Great Lakes water, as received in Key West, Florida.

4.2 Seawater and Great Lakes Water Properties – Deoxygenated

Both seawater and lake water were deoxygenated to 0.2 mg/L by sparging with nitrogen prior to transfer from the treatment tank to the exposure trough. Nitrogen bubbling continued during transfer to the exposure trough. Dissolved oxygen levels in the exposure trough were measured daily (Monday-Friday) and nitrogen was bubbled through the exposure trough in an effort to maintain DO levels to below 1.0 mg/L as required. Dissolved oxygen data for the seawater and lake water exposure troughs are shown in Figure 14 and Figure 15, respectively. The pH in deoxygenated seawater ranged from 7.91 to 8.37, while pH in deoxygenated lake water ranged from 7.85 to 8.98.



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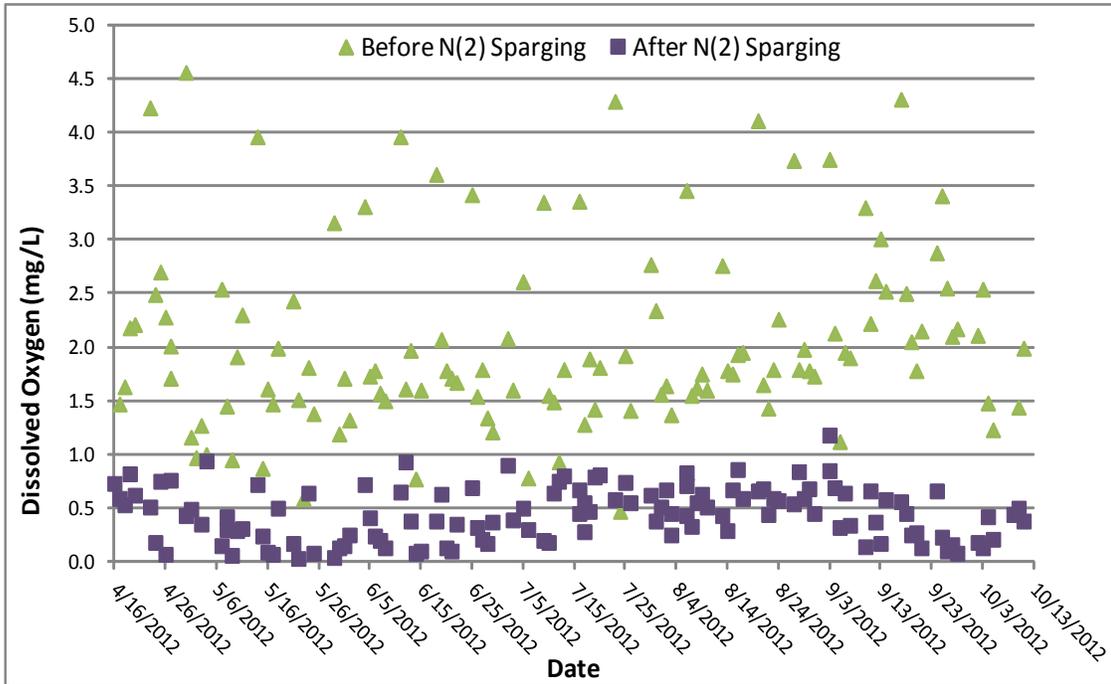


Figure 14. Dissolved oxygen content of seawater in deoxygenated exposure trough.

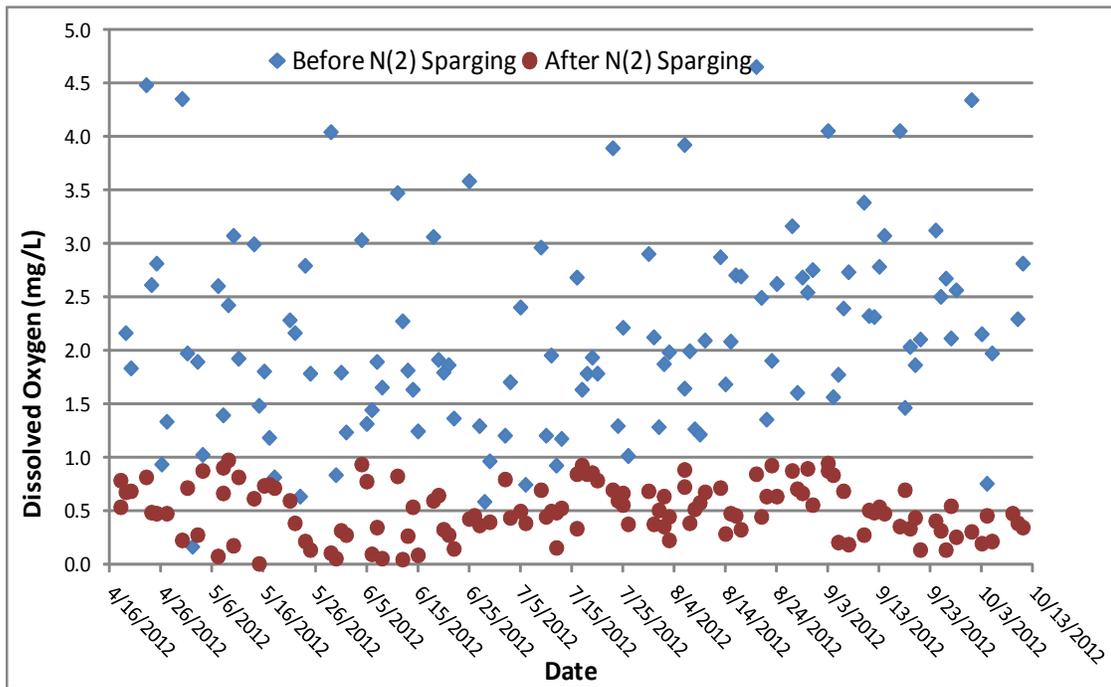


Figure 15. Dissolved oxygen content of lake water in deoxygenated exposure trough.



4.3 Seawater and Great Lakes Water Properties – Chlorinated

Following the initial addition of the chlorine solution to the respective treatment tank, it was clear that the calculated volumes of solution to be added were not sufficient to achieve the desired oxidant residual concentration of 10mg/L, as seen in the data from 16 April 2012. This was due to a combination of volatilization upon transfer, which affected seawater and Great Lakes water and chlorine demand of the water, which primarily affected the Great Lakes water.

Chlorine degradation begins immediately upon contact with the medium to be treated and testing is time sensitive, making consistent results on multiple specimens difficult. In order to adjust the volume to be added, chlorine demand tests were performed upon arrival of every lake water shipment. Identical tests were performed on seawater immediately prior to every subsequent fill cycle. Residual chlorine concentrations for seawater and lake water are given in Table 4.

Table 4. Residual chlorine concentrations in treatment tanks and exposure troughs.

Seawater			Lake Water		
Fill Date	Residual Chlorine (Treatment Tank)	Residual Chlorine (Exposure Trough)	Fill Date	Residual Chlorine (Treatment Tank)	Residual Chlorine (Exposure Trough)
16-Apr	1.6	-	18-Apr	-	-
30-Apr	11.6	-	2-May	10	6.0
14-May	10	5.4	15-May	9.8	8.0
29-May	10.8	8.2	29-May	14.8	4.4
11-Jun	12	8.2	12-Jun	12	4.5
25-Jun	16	6.6	26-Jun	16	4.2
9-Jul	16.4	6.8	12-Jul	15.4	5.9
23-Jul	14.2	6.8	25-Jul	11.2	2.9
6-Aug	13.8/15.6*	4.0/5.2*	7-Aug	11.4/12.8*	2.3/3.0*
20-Aug	15.2/16.8*	5.9/6.2*	21-Aug	15.5/16.5*	5.8/7.0*
4-Sep	12.8/13.4*	5.6/5.6*	4-Sep	14.0/14.8*	5.4/5.8*
17-Sep	14.0/15.6*	7.8/8.2*	18-Sep	13.4/13.2*	5.2/5.6*
1-Oct	18.1/18.2*	8.8/9.7*	2-Oct	10.45/17.6*	8.24/9.44*

*Until 06 August only free chlorine was measured in the treatment tank and exposure trough. After 06 August, both free chlorine (first value) and total chlorine (second value) were measured.

4.4 Seawater and Great Lakes Water Properties – Chlorine Dioxide

Similar to chlorine additions, the initial addition of the calculated volumes of chlorine dioxide solution to the respective treatment tank were not sufficient to achieve the desired oxidant residual concentration of 5 mg/L. This was especially true for the Great Lakes water, due to chlorine dioxide demand and the high volatility of the chlorine dioxide in the solution. The volatility component of chlorine dioxide loss was also a factor in seawater.

In order to adjust the volume to be added, chlorine dioxide demand tests, similar to the chlorine demand tests were performed upon arrival of every lake water shipment. These tests were also performed on seawater immediately prior to every fill cycle. Four cycles into the test, the method of chlorine dioxide addition was changed to siphoning the concentrated chlorine dioxide solution from the bottle in which it was supplied by the manufacturer to the trough to reduce atmospheric exposure and turbulence that volatilized the solution. This aided in retention of the chlorine dioxide. Residual chlorine dioxide concentrations for seawater and lake water are given in Table 5.

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Table 5. Residual chlorine dioxide concentrations in treatment tanks and exposure troughs.

Seawater			Lake Water		
Fill Date	Residual Chlorine (Treatment Tank)	Residual Chlorine (Exposure Trough)	Fill Date	Residual Chlorine (Treatment Tank)	Residual Chlorine (Exposure Trough)
16-Apr	1.93	-	18-Apr	-	-
30-Apr	5.50	2.02	2-May	4.28	0.60
14-May	5.50	2.73	15-May	4.84	2.97
29-May	5.50*	3.83	29-May	8.78*	2.31
11-Jun	4.53	2.23	12-Jun	5.48	2.72
25-Jun	10.78	4.05	26-Jun	11.00	3.87
9-Jul	9.30	2.61	12-Jul	6.64	1.50
23-Jul	7.20	3.49	25-Jul	6.52	2.11
6-Aug	6.38	2.80	7-Aug	9.04	3.31
20-Aug	8.92	3.54	21-Aug	9.02	1.61
4-Sep	6.88	3.74	4-Sep	8.56	3.30
17-Sep	7.58	4.26	18-Sep	5.62	2.73
1-Oct	5.17	1.81	2-Oct	8.08	2.14

*Method of chlorine dioxide addition changed on these dates to siphoning to reduce turbulence and atmospheric contact. All subsequent treatments were added by this method.

Chlorine dioxide reacts with and is consumed by dissolved organic carbon and organic particulates. The lake water, as delivered was tea-colored, which varied in shades over the course of the testing. This coloration is indicative of dissolved and particulate organics. In order to determine if particulate or filterable matter was significant, quantities of lake water were filtered through a 0.22 micron filter and subjected to the chlorine demand test concurrently with unfiltered water. The differences in demand between the filtered and unfiltered water were negligible, indicating the demand was due to dissolved, rather than particulate, organic matter.

4.5 Seawater – Comparison of Treatments under Each Condition on Each Substrate

In the following sections, the average mass loss of each triplicate group of specimens is presented where applicable. Since mass loss is dependent on the size of the specimen, in this case 3-inches x 2-inches x 1/8-inch (except where noted) the calculated value has been normalized to a corrosion rate expressed in mils per year (mpy). However, both average mass loss and corrosion rates are presented in the respective tables for each material.

4.5.1 Uncoated Steel

The data in Table 6 indicates that in an untreated humid seawater environment, uncoated mild steel experienced an average corrosion rate of 0.63 mpy. This low value is supported by the relatively small amount of corrosion product evident in the typical pre-cleaning photograph of the specimen in Figure 16. Of the three treatment methods investigated, chlorination resulted in the lowest average corrosion rate at 2.75 mpy. Corrosion rates for specimens in deoxygenated seawater and chlorine dioxide treated seawater were 8.06 and 9.10 mpy, respectively. From the amount of corrosion product on the deoxygenated and chlorine dioxide treated specimens in Figure 16, it is evident that the greatest amount of corrosion took place on the specimens in the deoxygenated and chlorine dioxide treated environments.

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Table 6. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in a humid seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.53	7.70	2.33	6.82
Average % Mass Loss	0.61%	8.82%	2.66%	7.81%
Average Corrosion Rate (mpy)	0.63	9.10	2.75	8.06

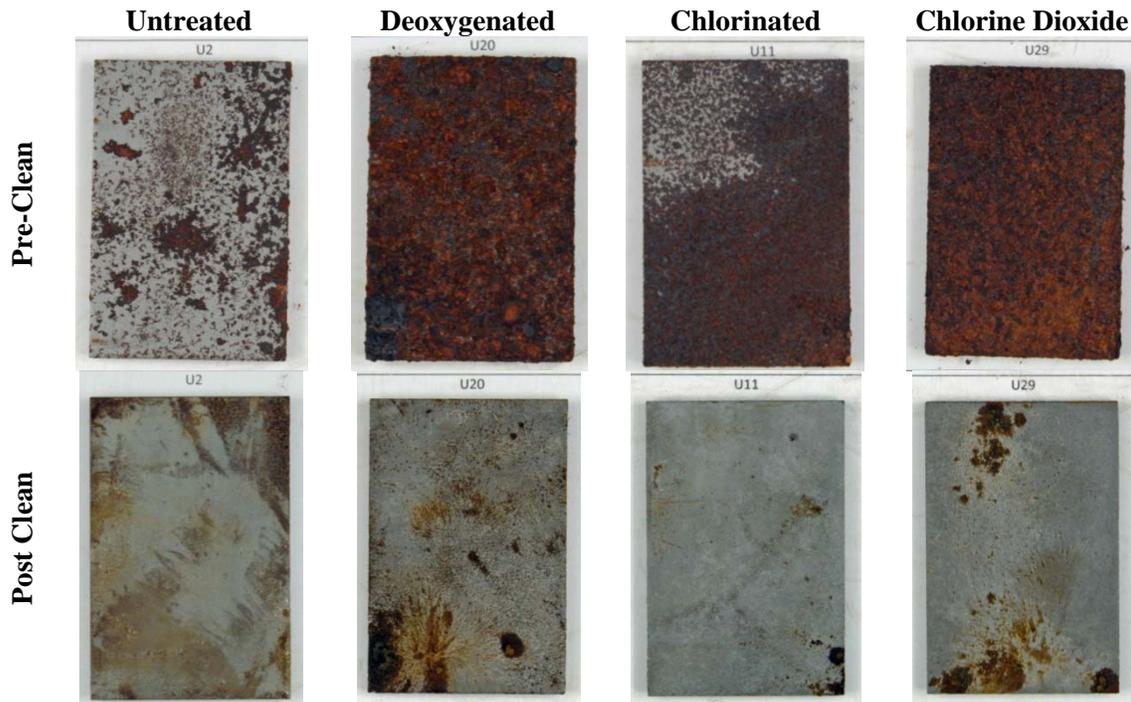


Figure 16. Seawater, humid environment, typical uncoated steel.

Alternate immersion in seawater has long been known to be a more aggressive environment than either atmospheric or constant immersion environments. Corrosion rates increased in the alternate immersion environment when compared to the humid environment for all treatments except chlorine dioxide. These values are given in Table 7. In the alternate immersion environment, the corrosion rates in the chlorinated and chlorine dioxide treated troughs were lower (7.97 mpy and 7.17 mpy, respectively) than in the untreated trough, where the corrosion rate was 10.12 mpy. Deoxygenated water was shown to be slightly more aggressive than untreated water, with a corrosion rate of 11.30 mpy. During the course of the test, the alternate immersion specimens in each of the seawater troughs developed a voluminous layer of ferric oxide, with more tightly adhered black ferrous oxide beneath. All were similar in appearance, before and after cleaning and typical specimens are shown in Figure 17.

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Table 7. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in an alternate immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	8.56	9.55	6.74	6.07
Average % Mass Loss	9.69%	10.96%	7.71%	6.93%
Average Corrosion Rate (mpy)	10.12	11.30	7.97	7.17



Figure 17. Seawater, alternate immersion environment, typical uncoated steel.

Average corrosion rates for uncoated steel specimens in a constant immersion environment are given in Table 8. The corrosion rates in the constant immersion environment were substantially reduced from those in the alternate immersion environment for all treatments. In constant immersion seawater, the specimens in the untreated trough experienced the highest corrosion rate, which was 2.74 mpy. This rate was slightly reduced in the chlorinated and chlorine dioxide treated troughs where the respective corrosion rates were 2.15 and 2.44 mpy. Deoxygenation had the greatest effect on corrosion rate in the constant immersion seawater environment, reducing the rate to 0.96 mpy. The uncoated steel specimens were similar in appearance regardless of treatment. The thin inner ferrous oxide layer was tightly adhered, while the outer, red ferric oxide layer was thin and was easily removed with a cloth or running water. Typical constant immersion specimens of uncoated steel are shown in Figure 18.

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Table 8. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in a constant immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	2.32	0.81	1.82	2.07
Average % Mass Loss	2.64%	0.92%	2.08%	2.35%
Average Corrosion Rate (mpy)	2.74	0.96	2.15	2.44



Figure 18. Seawater, constant immersion environment, typical uncoated steel.

4.5.2 Coated Steel

The differences in the mass loss or corrosion rates for coated steel panels are negligible regardless of environment. The greatest calculated corrosion rate for coated specimens was 0.08 mpy, for constant immersion specimens in a deoxygenated environment. There was no notable difference in appearance of the specimens prior to and following exposure, with the exception of staining from sediment and minor corrosion from a coating holiday. Mass loss and corrosion rate data for humid, alternate immersion and constant immersion exposure can be found in Table 9 through Table 11. Corresponding photographs of typical specimens for each of the conditions are shown in Figure 19 through Figure 21.

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Table 9. Average mass loss (g) and corrosion rate (mpy) for coated steel in a humid seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.04	0.05	0.04	0.05
Average % Mass Loss	0.05%	0.05%	0.04%	0.05%
Average Corrosion Rate (mpy)	0.05	0.05	0.04	0.05

Table 10. Average mass loss (g) and corrosion rate (mpy) for coated steel in an alternate immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.03	0.05	0.03	0.01
Average % Mass Loss	0.03%	0.06%	0.03%	0.01%
Average Corrosion Rate (mpy)	0.03	0.06	0.03	0.01

Table 11. Average mass loss (g) and corrosion rate (mpy) for coated steel in a constant immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.04	0.06	0.02	0.00
Average % Mass Loss	0.05%	0.07%	0.02%	0.00%
Average Corrosion Rate (mpy)	0.05	0.08	0.02	0.00

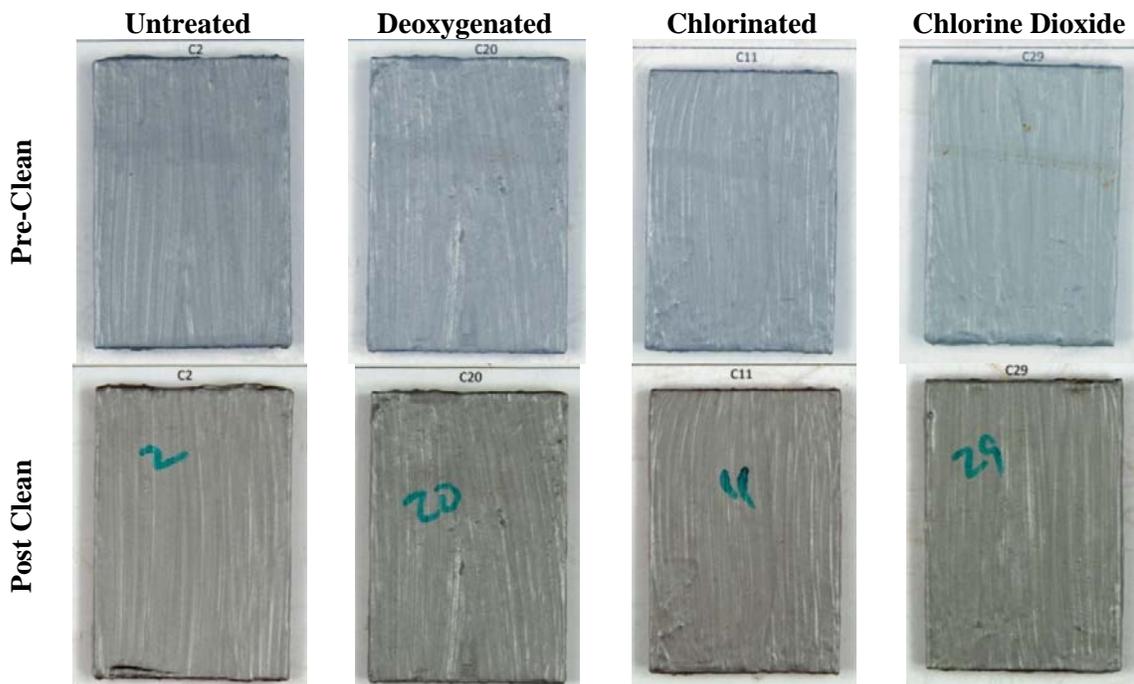


Figure 19. Seawater, humid environment, typical coated steel.



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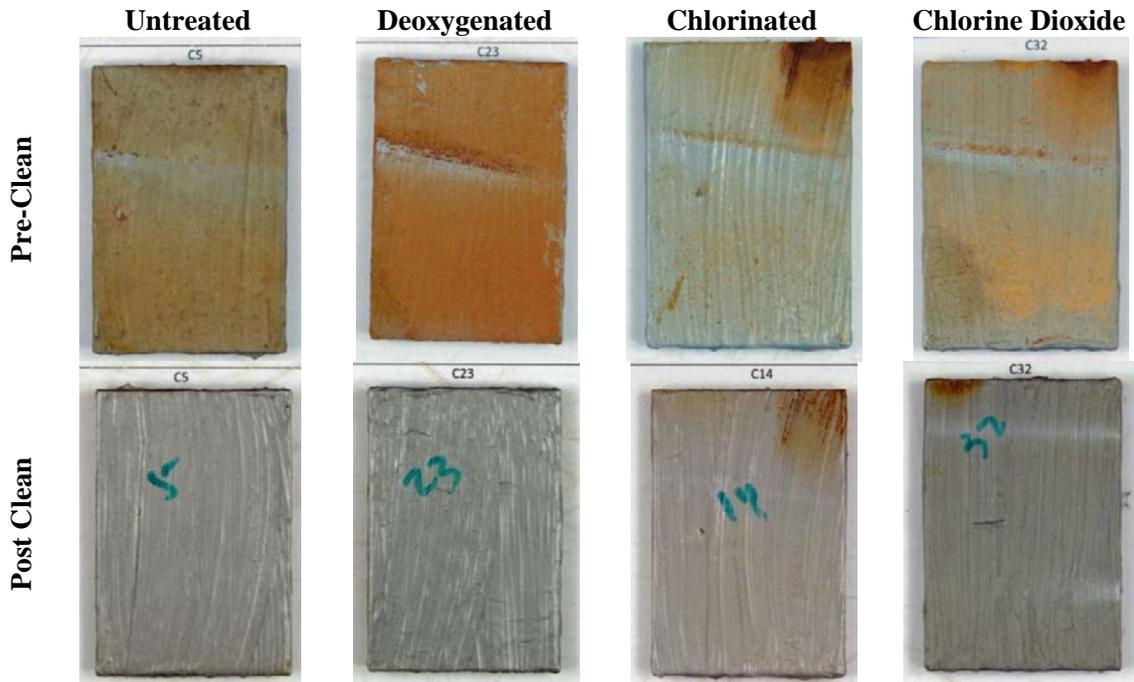


Figure 20. Seawater, alternate immersion environment, typical coated steel.

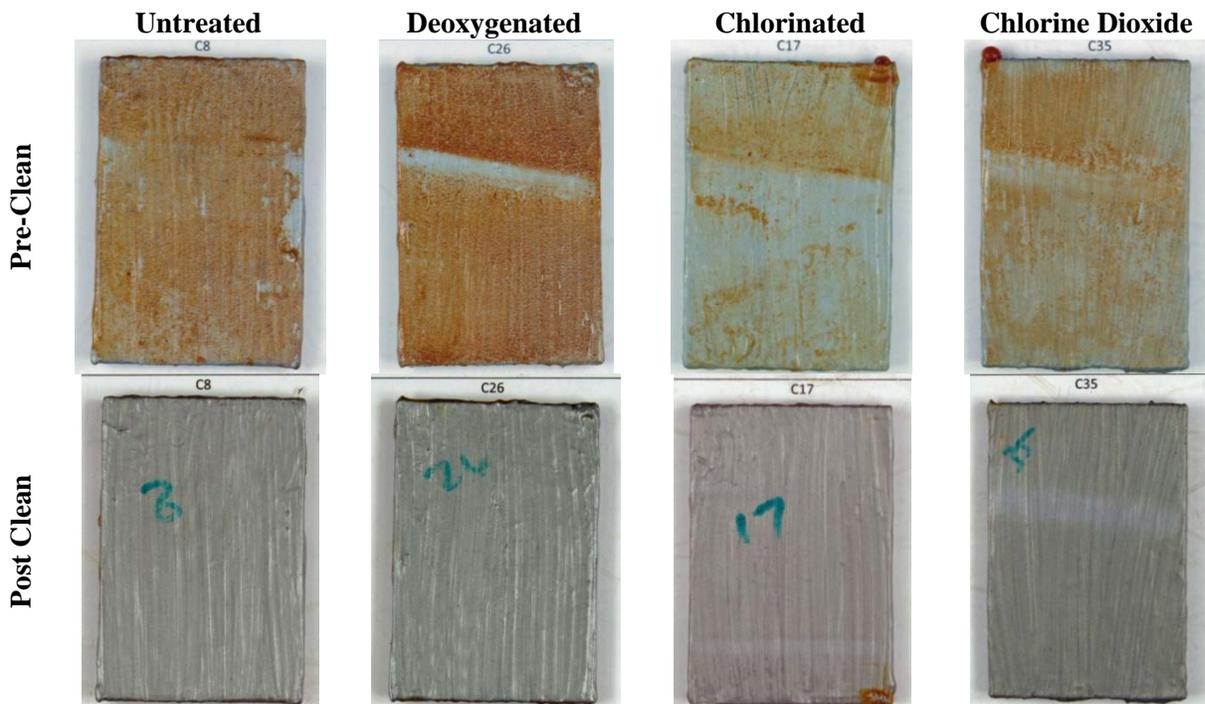


Figure 21. Seawater, constant immersion environment, typical coated steel.



4.5.3 Coated and Scribed Steel

On a coated and scribed substrate it is difficult to distinguish between the mass loss of the substrate and the mass loss of the coating. Additionally, moisture uptake at coating holidays (voids in coating) during immersion is not an uncommon phenomenon and may lead to calculated corrosion rates that are lower than actual corrosion rates. The coating breach created by the scribe may have provided an ingress for moisture absorption. Over time, this moisture can cause deterioration of the substrate-coating bond, resulting in coating disbondment. Therefore, corrosion behavior of coated and scribed specimens have been evaluated solely on visual inspection.

The visual data presented in Figure 22 shows typical specimens for each of the treatments in the humid environment. Chlorine dioxide treated specimens clearly experienced the most corrosion damage, followed by the specimens from the deoxygenated trough. The amount of corrosion product visible on the specimens in the untreated and chlorinated troughs is similar. Corrosion in the scribed area was tenacious and not easily removed. On cleaned substrate, marks from the mill bit used to cut the scribe were still visible.



Figure 22. Seawater, humid environment, typical steel, coated and scribed.

Voluminous corrosion products are evident on the typical alternate immersion specimens shown in Figure 23. The greatest amount of corrosion product was noted on the specimens exposed to deoxygenated seawater. This was followed by the specimens exposed to alternating wet and dry cycles of untreated seawater, chlorine dioxide treated seawater and chlorinated seawater. The post cleaning photographs show trace amounts of corrosion in the scribe and minor staining on the coating surface. However, based on the post cleaning photographs, there is no apparent increase in corrosion rate associated with these treatments.

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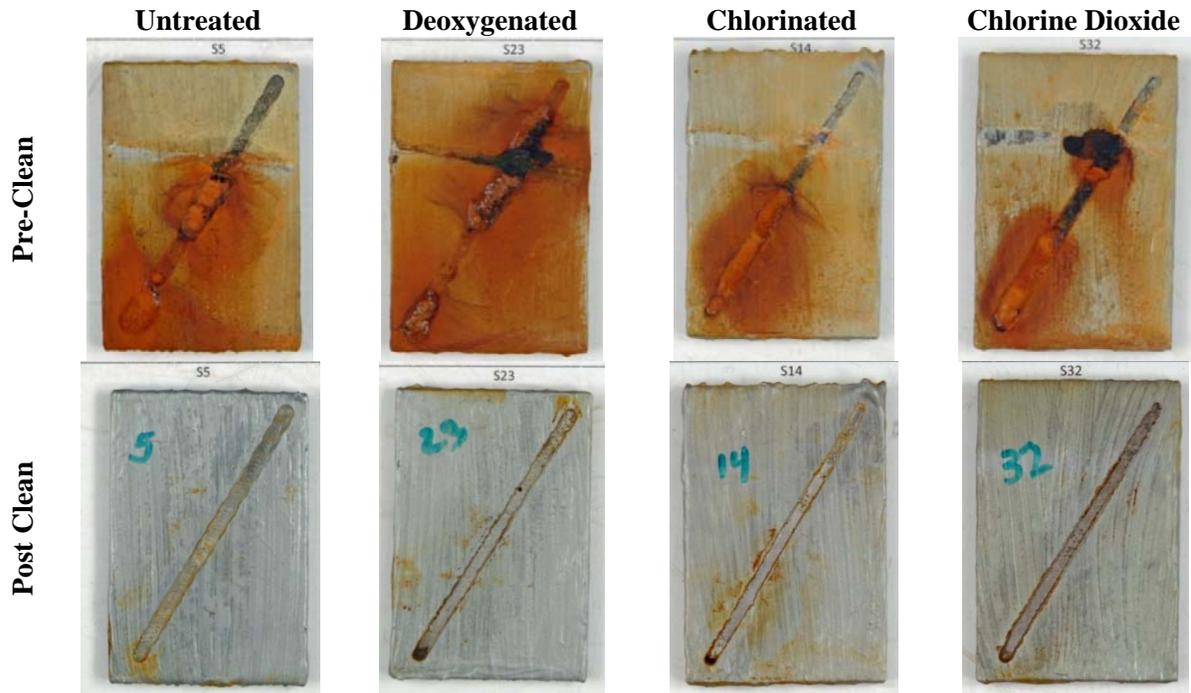


Figure 23. Seawater, alternate immersion environment, typical steel, coated and scribed.

Specimens subjected to constant immersion in seawater experienced that greatest amount of corrosion in the trough containing untreated seawater. This was followed by the specimens in deoxygenated seawater, chlorine dioxide treated seawater and chlorinated water. Typical specimens, shown in Figure 24, experienced no disbondment or undercutting of the coating at the scribe. Corrosion product was removed with a hydrochloric acid solution but traces remain on the specimens exposed to chlorinated and chlorine dioxide treated seawater. Based on the examination of the photographs, there is visual evidence that suggests that chlorine and chlorine dioxide may result in a decrease in corrosion rate.

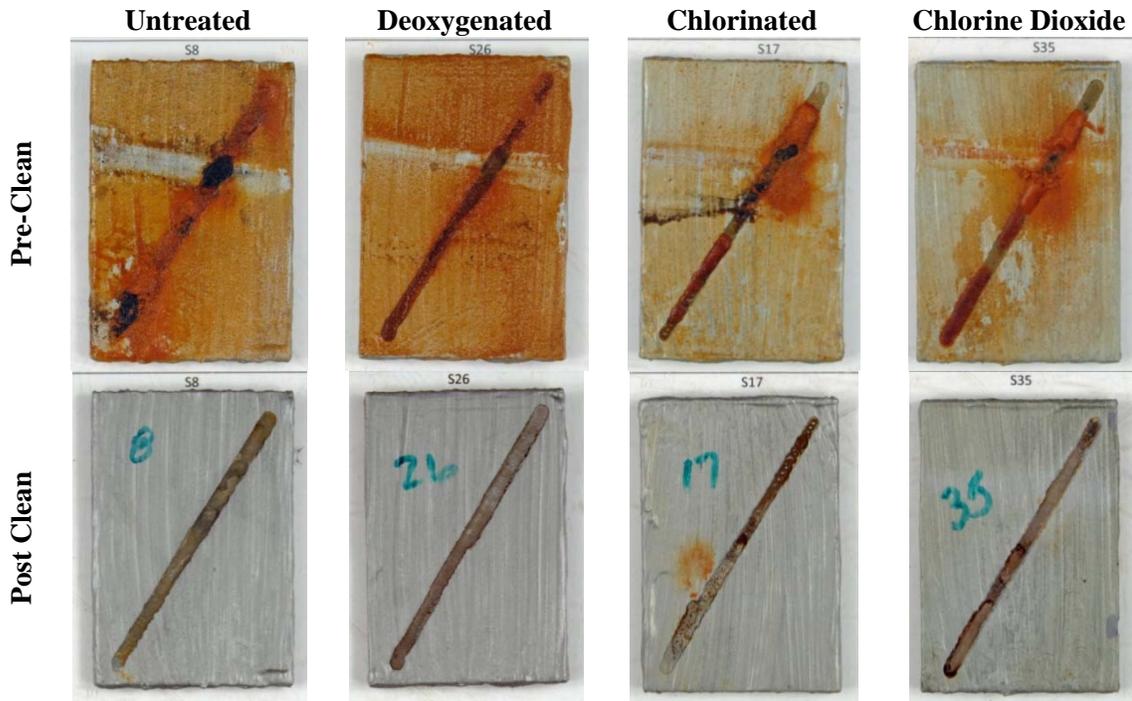


Figure 24. Seawater, constant immersion environment, typical steel, coated and scribed.

4.5.4 Coated, Scribed and Cathodically Protected Steel

The cathodically protected specimens were comprised of a series of components, which included the coating, fasteners, terminal lug and wiring that was susceptible to corrosion. Therefore, similar to the coated and scribed specimens, these specimens have been evaluated solely on visual inspections. Cathodically protected, coated and scribed specimens in the humid seawater environment were expected to show signs of corrosion similar to unprotected specimens as a result of the absence of a complete cathodic protection circuit including a conductive electrolyte. There is a visual similarity between the coated, scribed, unprotected specimens shown in Figure 22 and the coated, scribed, cathodically protected specimens shown in Figure 25. The specimens from the untreated and chlorinated troughs were nearly corrosion free, while the specimens from the deoxygenated trough and the trough treated with chlorine dioxide bore greater amounts of corrosion that spread, staining the coating. There was no immediate visual evidence of coating loss at the scribe on any of the panels exposed to the humid seawater environment, regardless of treatment. Actual corrosion in the scribed area was low enough that the marks from the mill bit used to create the scribe were still visible. In the humid environment, the visual data suggests that both deoxygenation and chlorine dioxide treatment result in increased corrosion rates.

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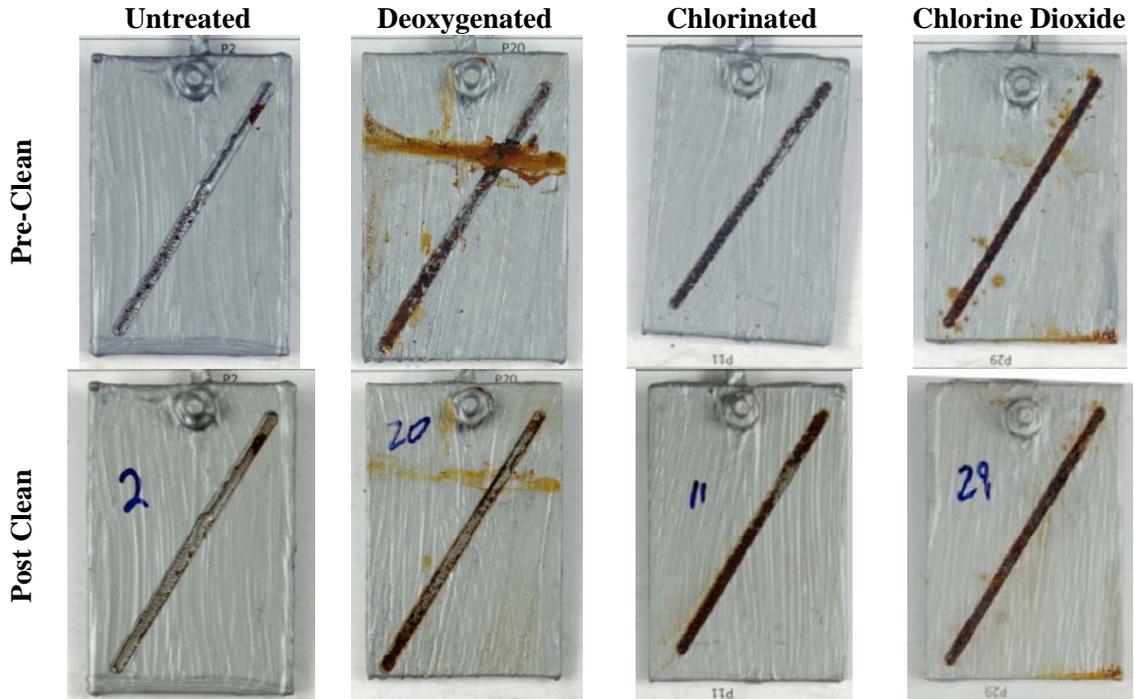


Figure 25. Seawater, humid environment, typical cathodically protected steel.

Typical specimens for each treatment in alternate immersion seawater are shown in Figure 26. The coated, scribed and cathodically protected alternate immersion specimens are different in appearance from the unprotected coated and scribed specimens, attributing that difference to the application of cathodic protection to the former. The pre-cleaned photographs of the specimens clearly show development of calcareous deposits, indicating that cathodic protection was functioning during the immersion segment of the cycle but these deposits appear to be broken or incomplete. It was concluded that the calcareous deposits were not fully formed at the time the dry cycle began, leaving some steel exposed in the moist atmosphere. The cessation of cathodic protection from the scribe area during the dry cycle allowed corrosion to occur on the areas where calcareous deposits had not yet formed. The reddish staining visible on the specimens was from corrosion product from the freely corroding specimens in the same trough and was completely removed upon specimen cleaning.



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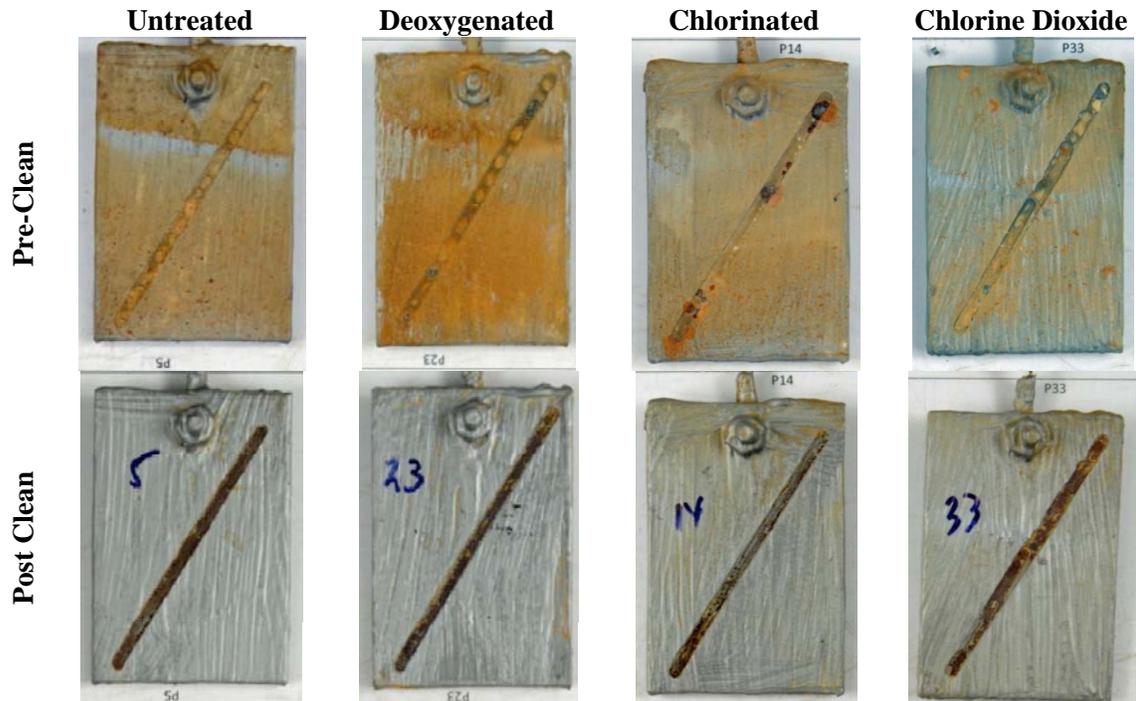


Figure 26. Seawater, alternate immersion environment, typical cathodically protected steel.

Typical constant immersion specimens are shown in Figure 27. The specimens clearly exhibit well-developed calcareous deposits covering the entire scribe area in the pre-cleaned state. Post cleaning images reveal scribes with little to no corrosion for three of the four treatments. For cathodically protected specimens in constant immersion in seawater, visual evidence suggests that there is no adverse effect caused by any of the treatments studied.



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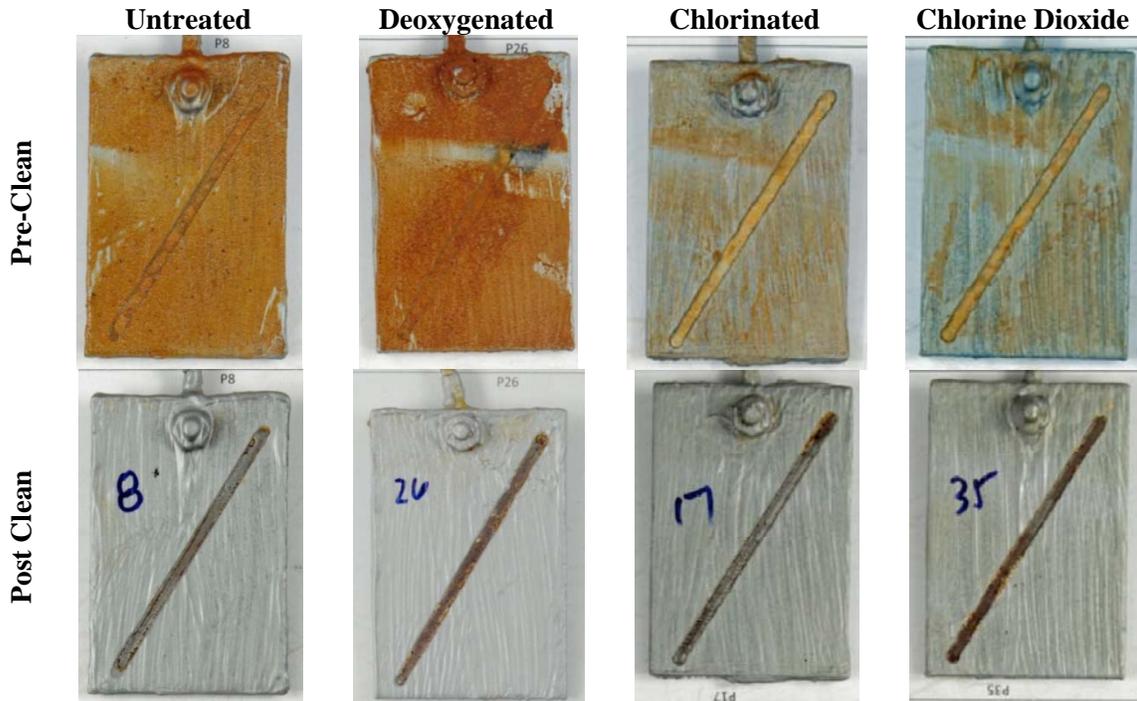


Figure 27. Seawater, constant immersion environment, typical cathodically protected steel.

4.5.5 Brass

Mass loss and subsequent corrosion rates, calculated for brass exposed to the humid seawater environment of troughs containing the different treatments are shown in Table 12. The specimens in the untreated trough experienced the lowest corrosion rate, 0.01 mpy. The corrosion rates of the specimens in the treated troughs increased as compared to the specimens in the untreated environment. Specimens in the three treatment troughs experienced similar corrosion rates of 0.13 mpy, 0.12 mpy and 0.13 mpy for deoxygenation, chlorination and chlorine dioxide treatment, respectively. These values are supported by the photographs in Figure 28, clearly showing increased corrosion products on the surface of the specimens deployed in the treatment troughs. These corrosion sites are from condensate or water dripped on the specimens during fill, drain or documentation procedures. Red colored zinc depleted areas are also clearly visible in the photographs showing the specimens, post cleaning.



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Table 12. Average mass loss (g) and corrosion rate (mpy) for brass in a humid seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.01	0.12	0.11	0.12
Average % Mass Loss	0.01%	0.12%	0.10%	0.11%
Average Corrosion Rate (mpy)	0.01	0.13	0.12	0.13

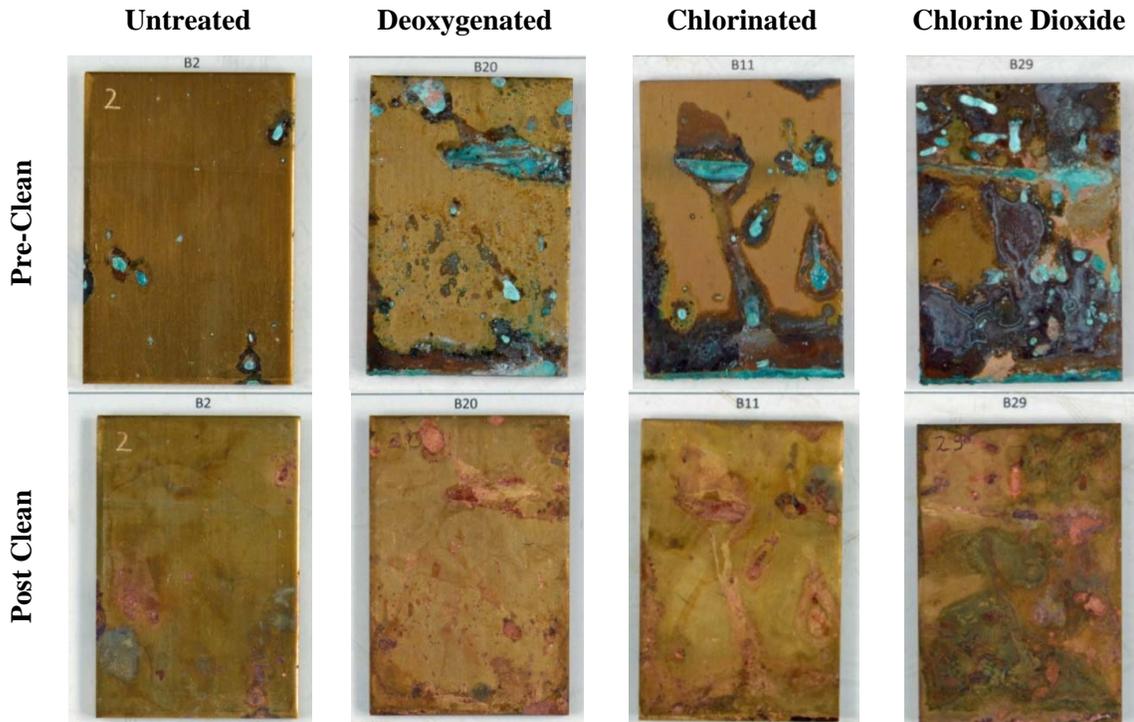


Figure 28. Seawater, humid environment, typical brass.

Brass specimens in the alternate immersion environment showed little difference in corrosion rates between treatments. Corrosion rates given in Table 13 ranged from 0.15 mpy for specimens in the untreated trough to 0.21 mpy for specimens in the deoxygenated trough. Prior to post immersion cleaning, the specimens in the chlorinated and chlorine dioxide treated troughs appeared to have a reddish color; however, all specimens, regardless of treatment were similar in appearance following cleaning. Typical brass specimens for each exposure are shown in Figure 29.

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Table 13. Average mass loss (g) and corrosion rate (mpy) for brass in an alternate immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.13	0.19	0.16	0.16
Average % Mass Loss	0.13%	0.18%	0.15%	0.15%
Average Corrosion Rate (mpy)	0.15	0.21	0.18	0.18

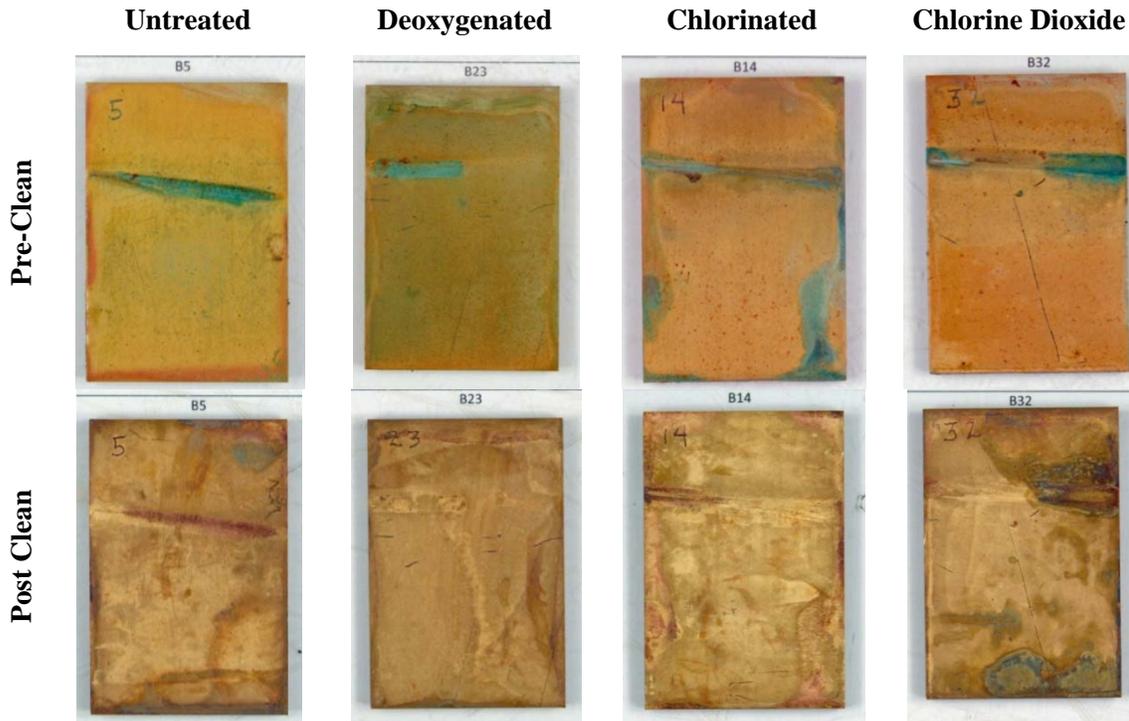


Figure 29. Seawater, alternate immersion environment, typical brass.

In the constant immersion environment, brass specimens in deoxygenated seawater experienced an average corrosion rate of 0.40 mpy, which was the highest rate of the four treatments studied. Specimens in chlorinated seawater were next with an average corrosion rate of 0.28 mpy. Specimens in the remaining conditions, untreated seawater and chlorine dioxide treated seawater experienced similar corrosion rates of 0.17 mpy and 0.14 mpy, respectively. These data are given in Table 14. These corrosion rates are supported by the photographs in Figure 30, which clearly shows a typical specimen from the deoxygenated trough having the greatest amount of corrosion product on the surface.

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Table 14. Average mass loss (g) and corrosion rate (mpy) for brass in constant immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.16	0.37	0.26	0.13
Average % Mass Loss	0.15%	0.34%	0.24%	0.12%
Average Corrosion Rate (mpy)	0.17	0.40	0.28	0.14

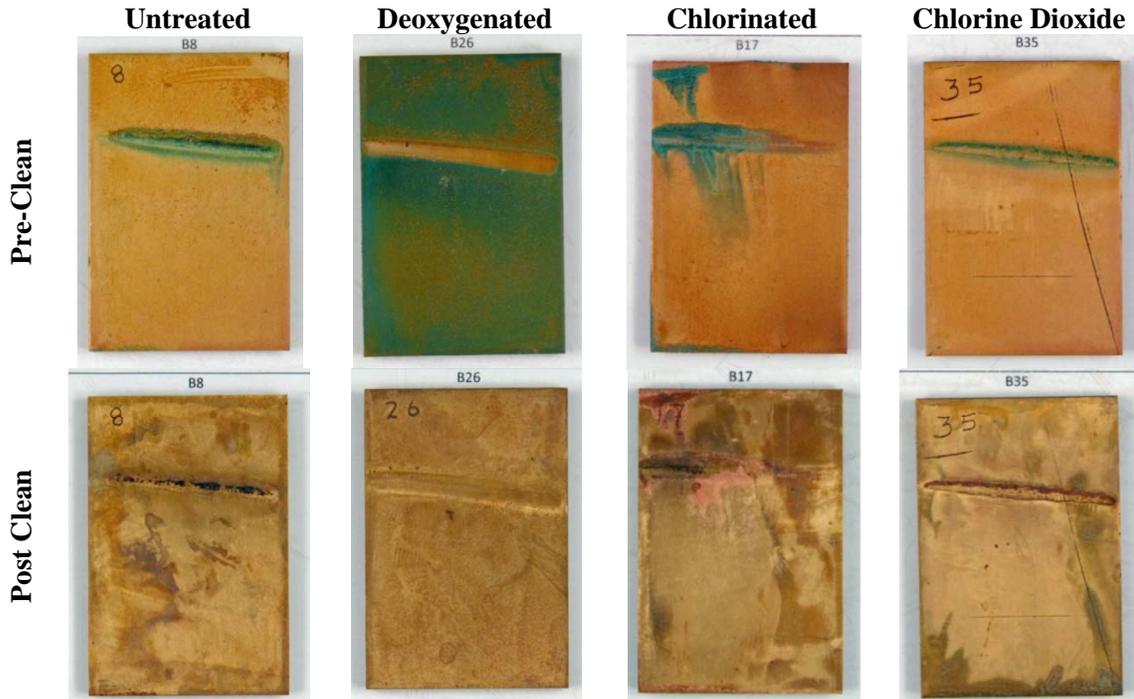


Figure 30. Seawater, constant immersion environment, typical brass.

4.5.6 Copper-Nickel

In the humid seawater environment, copper-nickel experienced the lowest average corrosion rate of 0.03 mpy in the trough containing untreated seawater. Specimens in the three treated troughs experienced mass losses, which resulted in all corrosion rates equal to 0.11 mpy. These rates, given in Table 15 correspond to the degree of corrosion noted in the photographs in Figure 31. The typical untreated specimen experienced corrosion only at the interface with the specimen support as evidenced by the copper chloride (patina) visible on the top part of the specimen. There are increased amount of copper chloride on the specimens exposed to the deoxygenated and chlorinated atmospheres, accounting for the increased mass loss. The specimens exposed to the chlorine dioxide treated environment bear a combination of copper chloride and a darker colored product, cupric oxide.



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Table 15. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in a humid seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.02	0.11	0.11	0.10
Average % Mass Loss	0.02%	0.09%	0.09%	0.09%
Average Corrosion Rate (mpy)	0.03	0.11	0.11	0.11

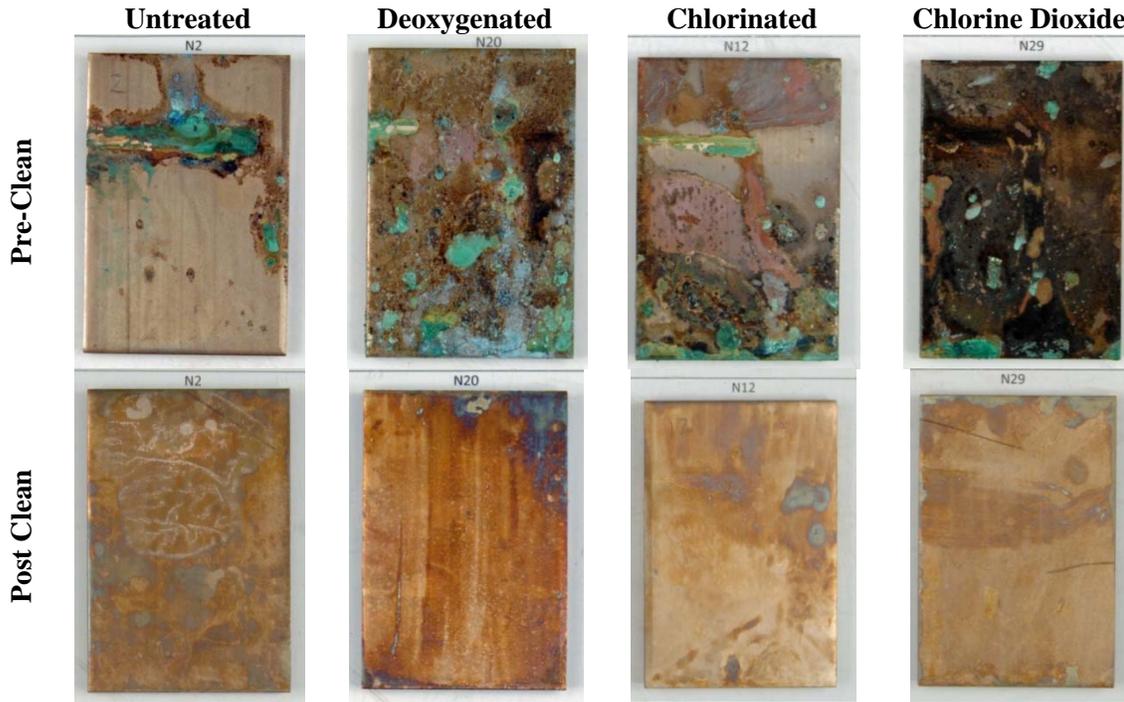


Figure 31. Seawater, humid environment, typical copper-nickel.

In the alternate immersion environment, the average corrosion rate of specimens in untreated seawater was calculated to be 0.17 mpy. This was the highest corrosion rate calculated for copper-nickel in alternate immersion and nearly a six-fold increase in the corrosion rate as compared to the humid seawater environment. Specimens in the treated troughs all experienced slightly lower corrosion rates, given in Table 16, than did the specimens in untreated seawater. Typical photographs showing the increased amount of copper-based corrosion product on the specimen exposed to alternate immersion in untreated seawater, as well as those in treated seawater, are shown in Figure 32.

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Table 16. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in an alternate immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.17	0.09	0.11	0.07
Average % Mass Loss	0.14%	0.07%	0.09%	0.06%
Average Corrosion Rate (mpy)	0.17	0.09	0.11	0.08

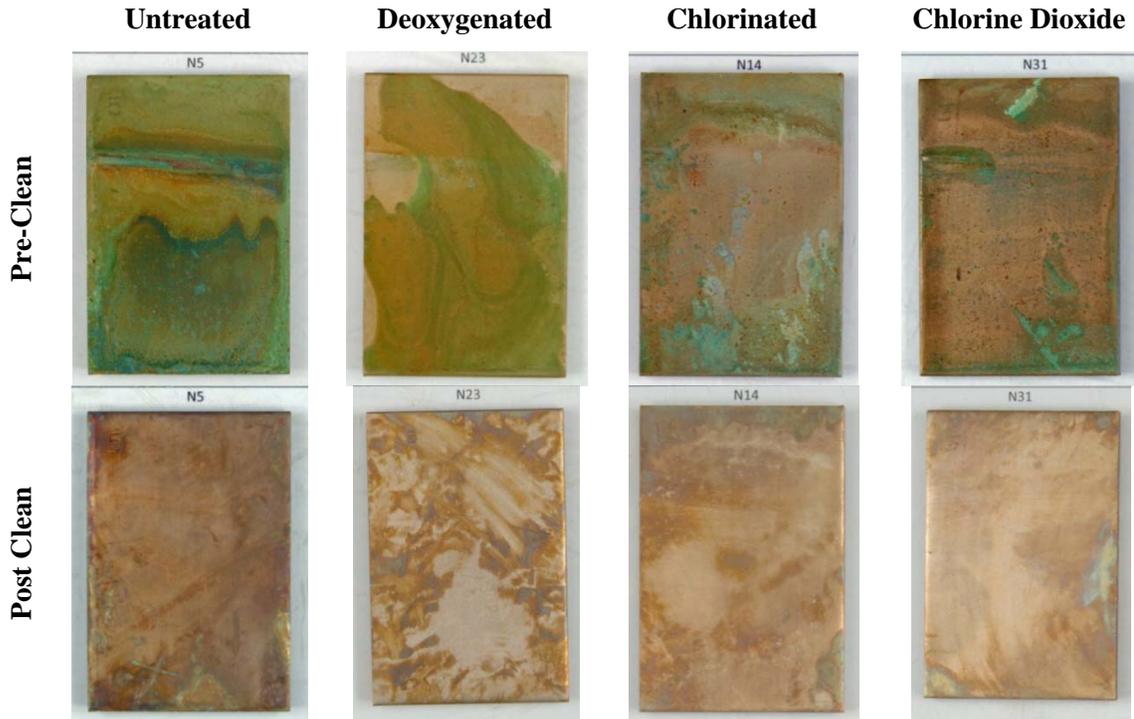


Figure 32. Seawater, alternate immersion environment, typical copper-nickel.

Average mass loss and resultant corrosion rates for copper-nickel in a constant immersion environment were similar to those in the alternate immersion environment. Calculated corrosion rates were 0.13 mpy for specimens in untreated and chlorinated seawater. These rates were reduced to 0.06 mpy for specimens in deoxygenated seawater and 0.07 mpy for specimens in seawater treated with chlorine dioxide. Mass loss and corrosion rate data for copper-nickel in constant seawater immersion are given in Table 17. Typical photographs showing copper-based corrosion products on the untreated and chlorinated specimens, as well as relatively corrosion free specimens from the deoxygenated and chlorine dioxide treated troughs are shown in Figure 33.

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Table 17. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in constant immersion seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.13	0.06	0.12	0.07
Average % Mass Loss	0.11%	0.05%	0.10%	0.06%
Average Corrosion Rate (mpy)	0.13	0.06	0.13	0.07

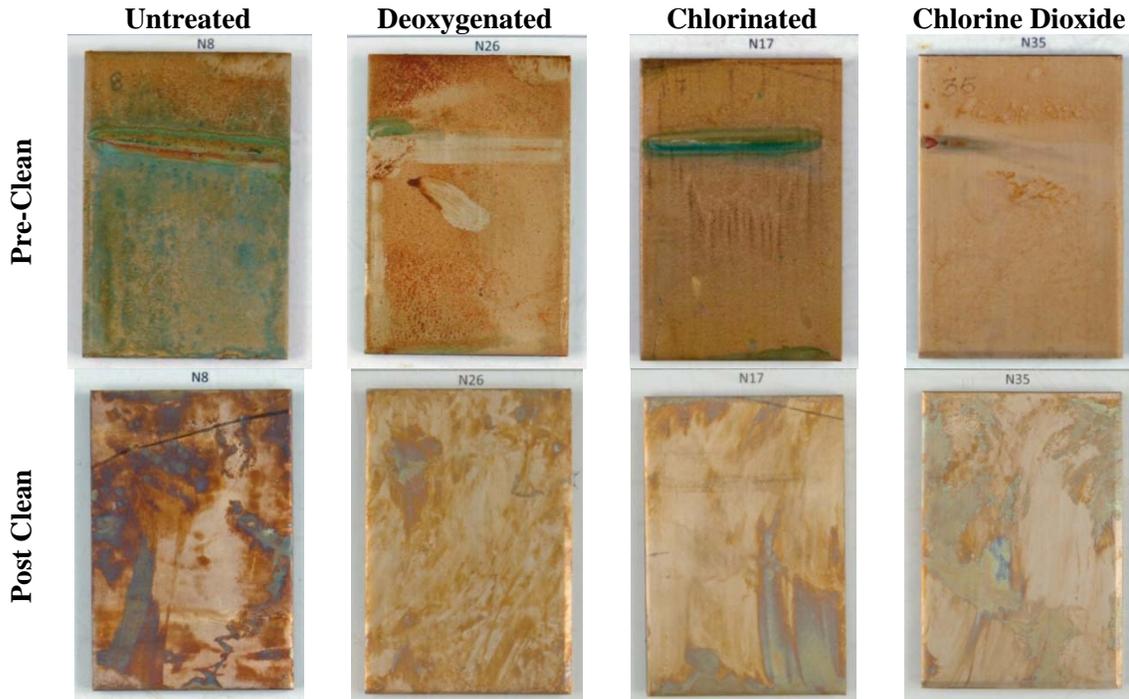


Figure 33. Seawater, constant immersion environment, typical copper-nickel.

4.5.7 Glyon® Gasket

Glyon® is a flexible polytetrafluoroethylene (PTFE) gasket material manufactured by Garlock, Palmyra, NY. All of the gasket material showed mass gains of less than 0.012 grams regardless of the environment combination tested. Such small differences, not exceeding 0.09% of the original mass, may be considered insignificant; however, the constant immersion specimens consistently experienced the lowest mass gain regardless of treatment. The mass increases in the humid and alternate immersion environments were similar. This data is given in Table 18. As the humid and alternate immersion specimens experienced forms of moisture (either immersion or condensation) alternating with dry periods, it is hypothesized that the mass gain may be the result of sediment, salt and other atmospheric particles that were allowed to dry on the surface and subsequently became adhered or trapped in the pits of the surface profile. Additionally, no cracking or change in flexibility of the material was noted under any conditions. Photographs representative of each triplicate set following cleaning are shown in Figure 34.

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Table 18. Average mass loss (g) and corrosion rate (mpy) for Glyon® gasket material in a seawater environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Humid	-0.011 -0.09%	-0.011 -0.08%	-0.005 -0.04%	-0.012 -0.09%
Alternate Immersion	-0.007 -0.05%	-0.012 -0.09%	-0.05 -0.04%	-0.010 -0.08%
Constant Immersion	-0.001 -0.01%	-0.001 -0.01%	-0.001 -0.01%	-0.001 -0.01%

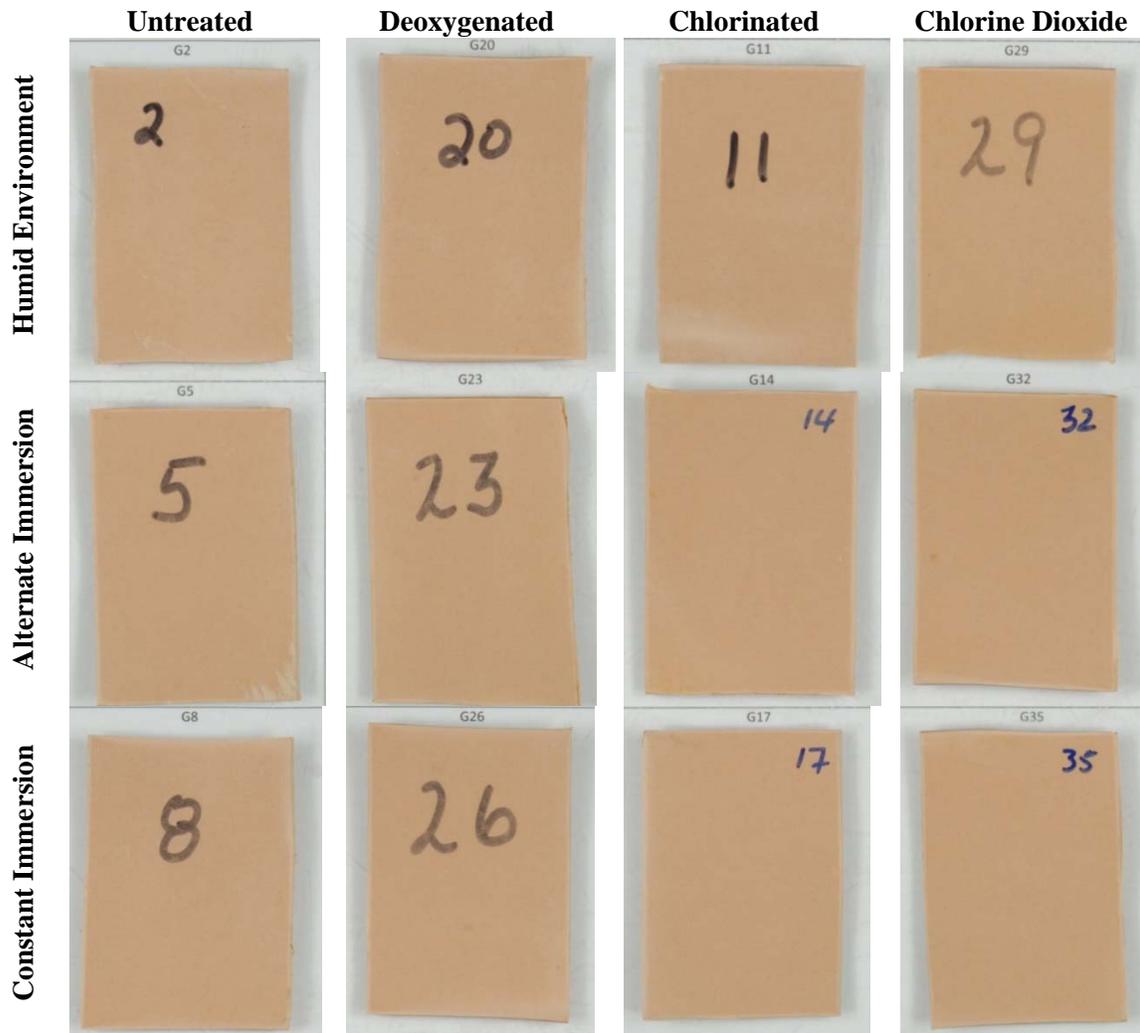


Figure 34. Seawater, typical Glyon® gasket specimens.

4.6 Great Lakes Water - Comparison of Treatments under Each Condition on Each Substrate

4.6.1 Uncoated Steel

The data in Table 19 indicate that mild steel in a humid environment above untreated lake water experienced an average corrosion rate of 0.38 mpy. That corrosion rate was reduced to 0.28 mpy in the

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atmosphere above deoxygenated lake water. These low values are supported by sparse amounts of corrosion products evident in the pre-cleaning photographs of typical specimens in Figure 35. The two specimens with the greater amounts of visible surface corrosion are typical of the chlorinated and chlorine dioxide treated troughs, where corrosion rates were calculated to be 0.56 mpy and 1.40 mpy, respectively. These values are in general agreement with the visual evidence presented in the photographs presented in Figure 35.

Table 19. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in a humid lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.32	0.23	0.48	1.18
Average % Mass Loss	0.38%	0.27%	0.55%	1.35%
Average Corrosion Rate (mpy)	0.38	0.28	0.56	1.40

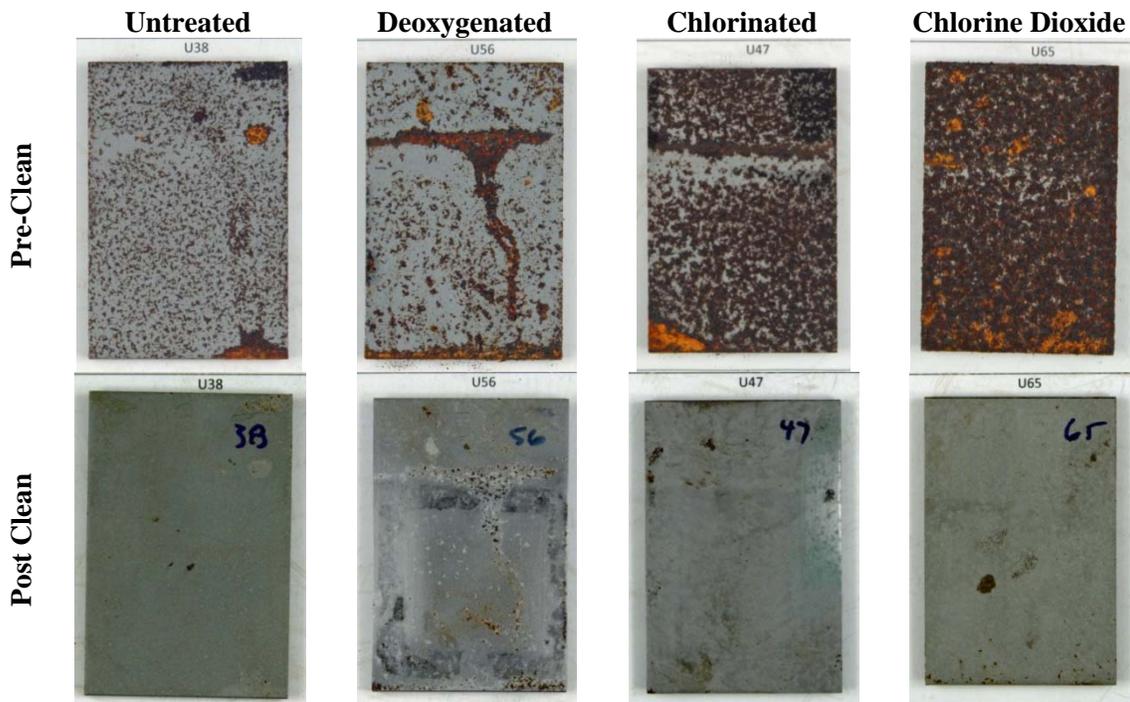


Figure 35. Great Lakes water, humid environment, typical uncoated steel.

Alternate immersion in Great Lakes water proved to be a more aggressive environment than either the humid or the constant immersion environment. The alternate immersion specimens in the deoxygenated environment experienced the lowest corrosion rate of 3.77 mpy. This was lower than the average rate of 5.59 mpy calculated for the alternate immersion specimens in the untreated trough. The addition of chlorine or chlorine dioxide resulted in increases in corrosion rate when compared to the specimens in the untreated trough. Rates for these treatments increased to 12.43 mpy and 10.01 mpy, respectively. These values are given in Table 20. During the course of the test, the alternate immersion specimens in each of the Great Lakes water troughs developed a voluminous layer of ferric oxide, which hardened during the dry alternate immersion cycles. Typical specimens are shown in Figure 36.

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Table 20. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in an alternate immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	4.73	3.19	10.51	8.47
Average % Mass Loss	5.47%	3.63%	12.06%	9.62%
Average Corrosion Rate (mpy)	5.59	3.77	12.43	10.02

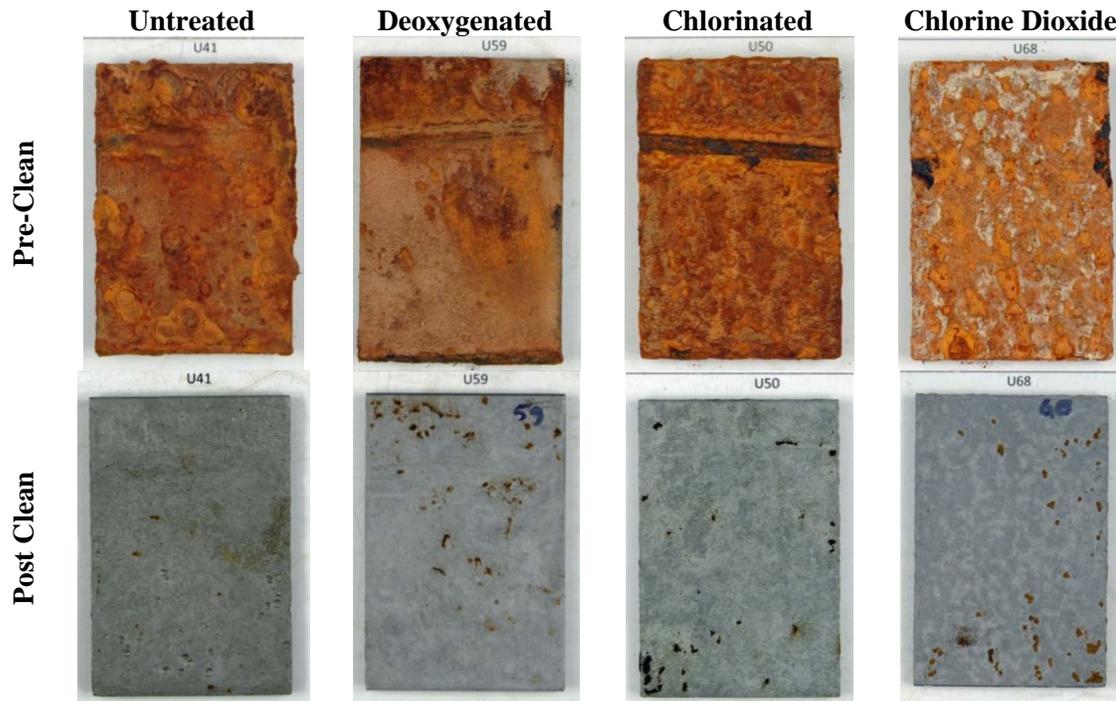


Figure 36. Great Lakes water, alternate immersion environment, typical uncoated steel.

Average corrosion rates for uncoated steel specimens in a constant immersion Great Lakes water environment are given in Table 21. Uncoated steel, in untreated lake water experienced an average corrosion rate of 2.23 mpy. Deoxygenation resulted in a decrease of this rate to 0.64 mpy. Chlorination had no effect, as the corrosion rate was 2.23 mpy, the same as in the untreated water. An increase was observed with chlorine dioxide treatment, resulting in the maximum rate of 2.87 mpy. The uncoated steel specimens were similar in appearance despite the method of treatment. The inner ferrous oxide layer was thin and tightly adhered. This layer can be seen where the outer layer sloughed off on the pre-cleaned chlorinated water specimen in Figure 37. The outer, red ferric oxide layer visible on the remaining specimens was easily removed with a cloth or running water.

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Table 21. Average mass loss (g) and corrosion rate (mpy) for uncoated steel in constant immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	1.89	0.54	1.88	2.43
Average % Mass Loss	2.18%	0.61%	2.15%	2.76%
Average Corrosion Rate (mpy)	2.23	0.64	2.23	2.87

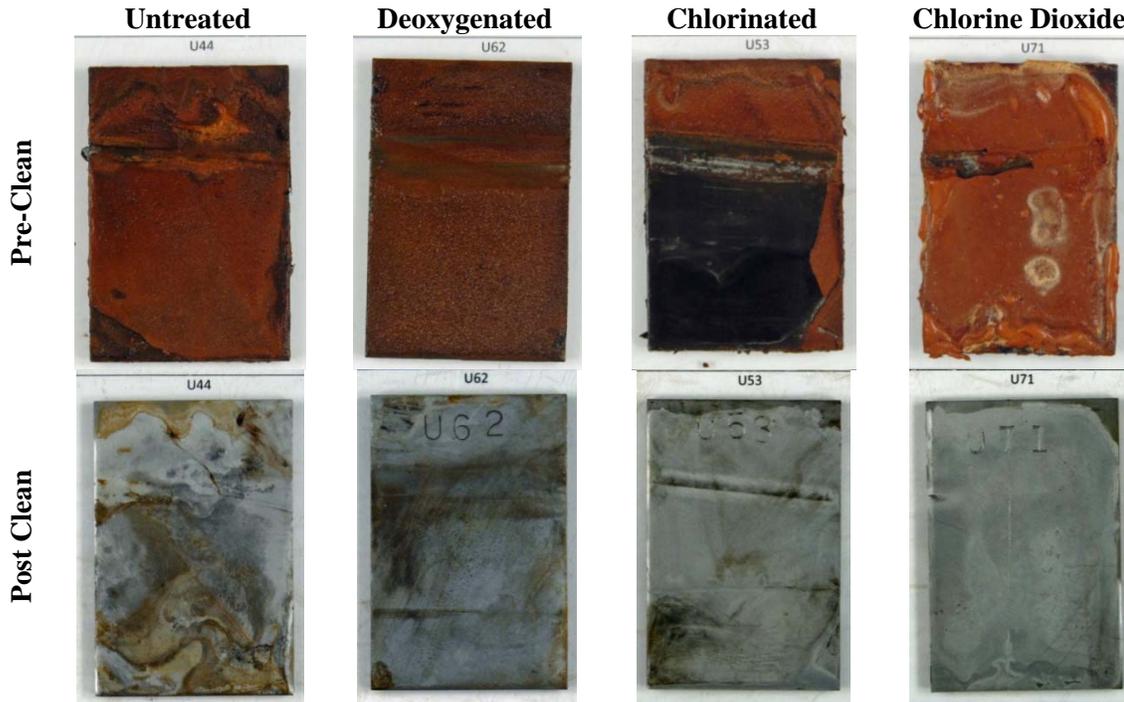


Figure 37. Great Lakes water, constant immersion environment, typical uncoated steel.

4.6.2 Cathodically Protected Steel

Due to the lack of a complete cathodic protection circuit, the cathodically protected specimens in the humid environment experienced corrosion similar to the unprotected specimens. The data presented in Table 22 indicate that the greatest loss was noted in the chlorine dioxide treated trough where the specimens experienced an average corrosion rate of 1.67 mpy. Corrosion rates were reduced in the deoxygenated and chlorine dioxide treated troughs, where specimens experienced similar rates of 0.33 and 0.30 mpy, respectively. The specimens in the untreated trough saw an average corrosion rate of 1.11 mpy. The comparative corrosion rates noted in Table 22 are mirrored in the photographs presented in Figure 38. The specimen exposed to the chlorine dioxide environment clearly shows the greatest amount of surface corrosion. The lighter central area was that part of the specimen that was shielded by the anode. Both the untreated and the deoxygenated specimens had concentrated areas of corrosion near the edges where intermittent wetting may have occurred during fill cycles.

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Table 22. Average mass loss (g) and corrosion rate (mpy) for cathodically protected steel in a humid lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.94	0.28	0.26	1.41
Average % Mass Loss	1.09%	0.32%	0.30%	1.62%
Average Corrosion Rate (mpy)	1.11	0.33	0.30	1.67

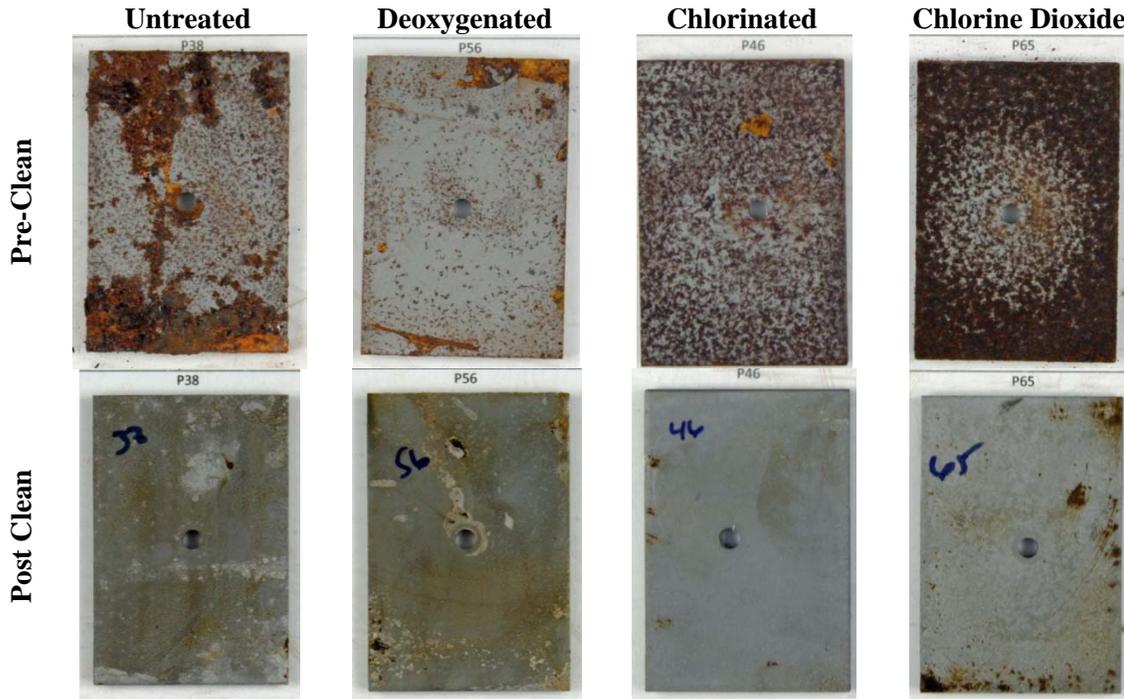


Figure 38. Great Lakes water, humid environment, typical cathodically protected steel.

The corrosion rates for cathodically protected steel in an alternate immersion environment were an improvement over the rates calculated for unprotected, uncoated steel in the lake water environment. Cathodically protected specimens in the alternate immersion Great Lakes water environment all experienced corrosion rates equal to or lower than 0.71 mpy and these are presented in Table 23. Specimens in untreated lake water, in an alternate immersion environment, experienced slightly lower corrosion rates of 0.51 mpy. Chlorination and chlorine dioxide treatment reduced corrosion rates below those of specimens in untreated water to 0.39 mpy and 0.34 mpy, respectively. Visually, the specimens have a similar appearance despite differences in treatment. Localized corrosion on the edges the specimens in untreated and deoxygenated lake water contributed to the higher corrosion rates. This localized corrosion is visible on the typical specimens shown in Figure 39. Alternating wet and dry cycles caused layers of sediment to deposit on the upward facing side of the specimens. This resulted in a sandy appearance, which was easily cleaned following removal. This lighter coloration was also noted on the all lake water alternate immersion specimens to varying degrees, but was most noticeable on the cathodically protected specimens.

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Table 23. Average mass loss (g) and corrosion rate (mpy) for cathodically protected steel in an alternate immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.43	0.60	0.33	0.29
Average % Mass Loss	0.50%	0.70%	0.38%	0.33%
Average Corrosion Rate (mpy)	0.51	0.71	0.39	0.34

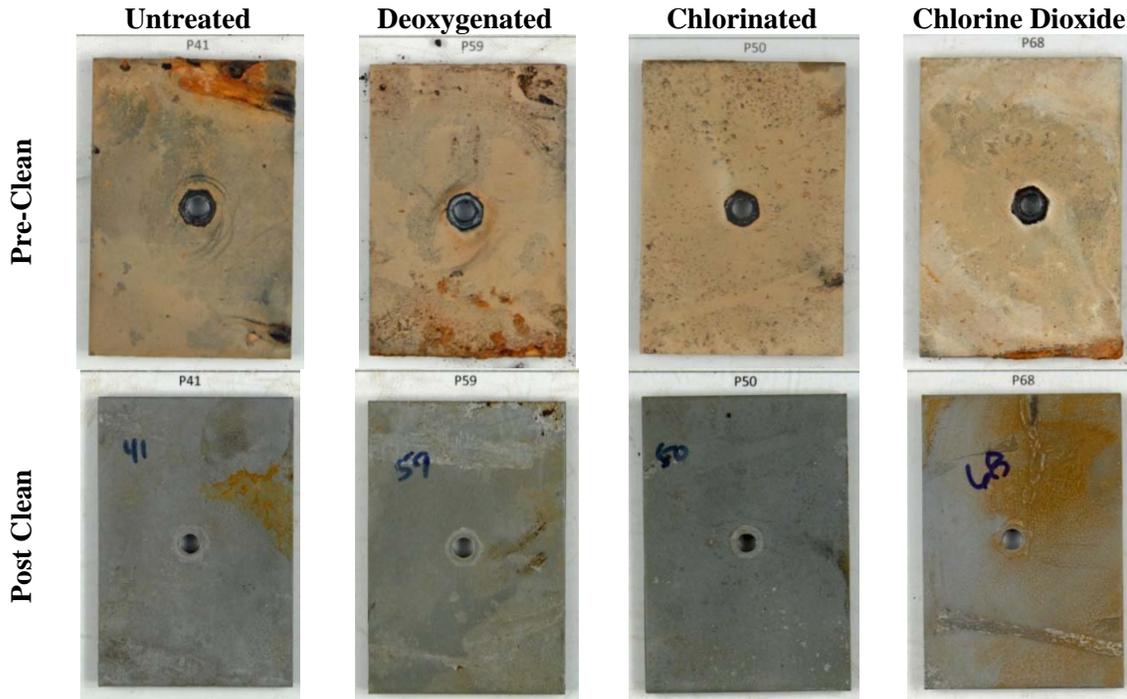


Figure 39. Great Lakes water, alternate immersion environment, typical cathodically protected steel.

Corrosion rates of cathodically protected steel in constant lake water immersion were similar regardless of treatment condition; all equal to or lower than 0.10 mpy. The differences between these values, given in Table 24, may be considered negligible within the limitations of the scope of this work. The images of typical specimens, shown in Figure 40, reveal little difference in the appearance of the specimens following removal, disassembly and cleaning. The rust colored staining on the surfaces in the pre-cleaning photographs was more the result of residue from corrosion products of other iron-based specimens in the same trough, than the result of corrosion of the cathodically protected specimens.

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Table 24. Average mass loss (g) and corrosion rate (mpy) for cathodically protected steel in constant immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.05	0.04	0.04	0.09
Average % Mass Loss	0.05%	0.04%	0.05%	0.10%
Average Corrosion Rate (mpy)	0.06	0.04	0.05	0.10

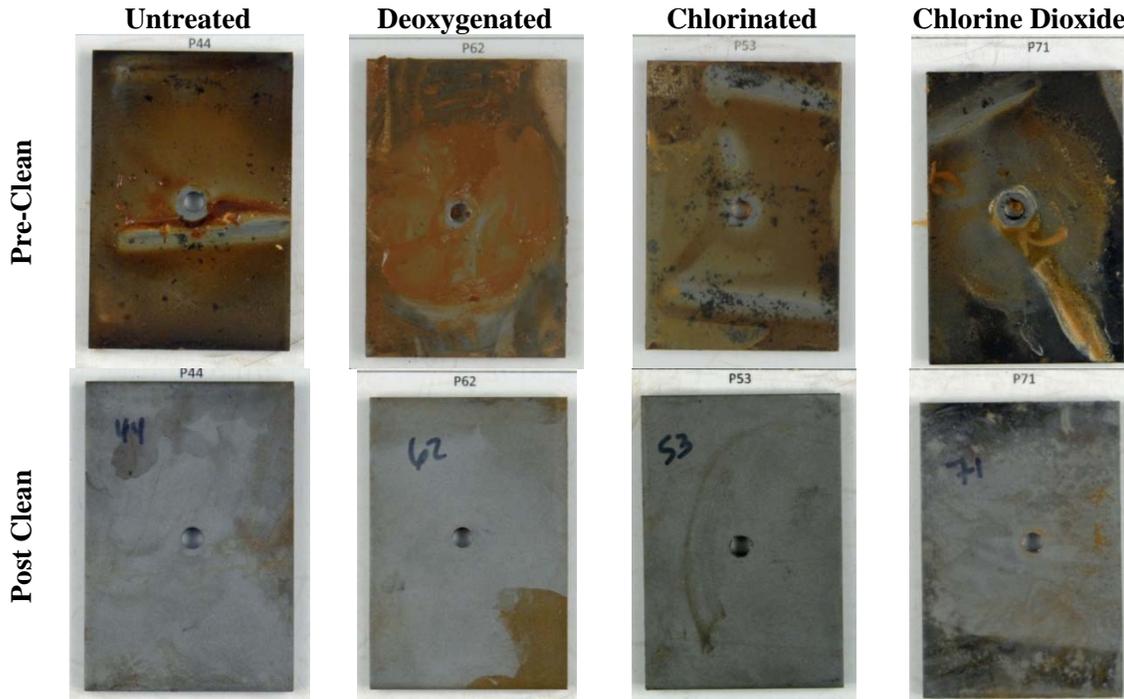


Figure 40. Great Lakes water, constant immersion environment, typical cathodically protected steel.

4.6.3 Cast Iron

The corrosion rates of cast iron in the humid lake water environment are given in Table 25. The corrosion rate above untreated lake water was 0.39 mpy. Rates for specimens exposed to treated environments ranged from 0.15 mpy above chlorinated lake water to 0.80 mpy above lake water treated with chlorine dioxide. The 0.15 mpy rate in the environment above chlorinated lake water represents a decrease in corrosion rate with treatment, while deoxygenated and chlorine dioxide treated water resulted in increases. The corrosion shown in the typical pre-cleaning photographs of Figure 41 was surface rust and easily removed during cleaning.



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Table 25. Average mass loss (g) and corrosion rate (mpy) for cast iron in a humid lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.33	0.37	0.13	0.68
Average % Mass Loss	0.11%	0.13%	0.04%	0.23%
Average Corrosion Rate (mpy)	0.39	0.44	0.15	0.80

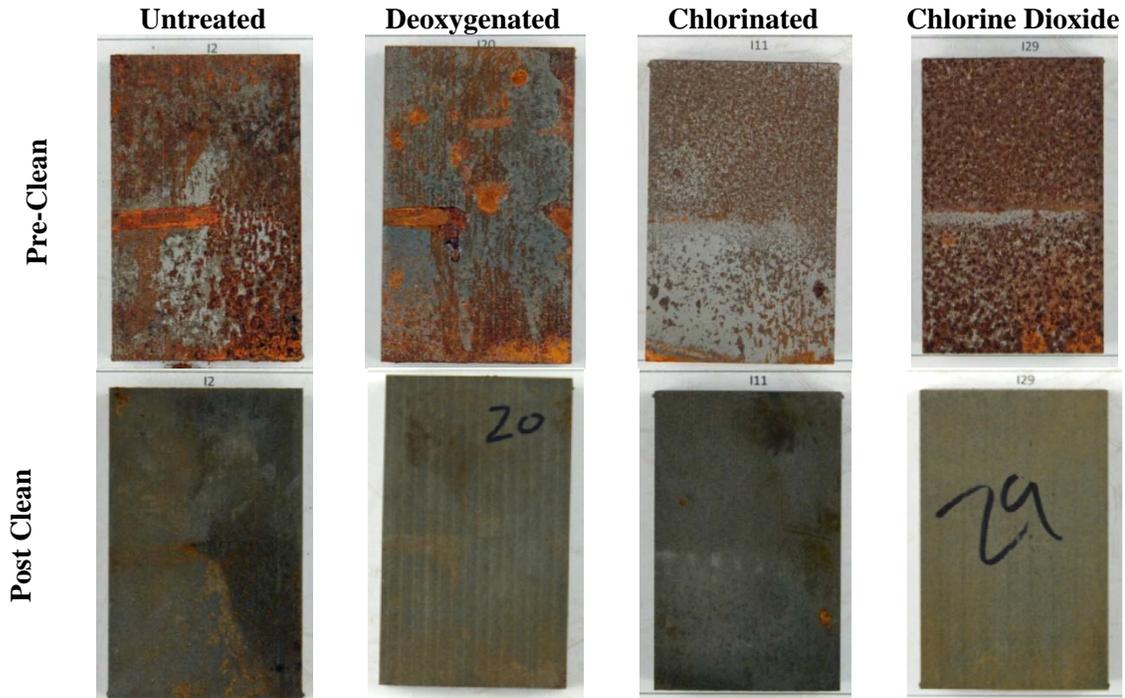


Figure 41. Great Lakes water, humid environment, typical cast iron.

Corrosion rates for cast iron in alternate immersion lake water environments were significantly higher than humid environment corrosion rates. An average corrosion rate of 6.66 mpy was calculated for specimens in untreated lake water. The data presented in Table 26 indicate that all active treatments resulted in decreased corrosion rates ranging from 5.42 mpy for chlorine dioxide treatment to 3.99 mpy in deoxygenated lake water. Corrosion products on each of the specimens were the reddish-orange color of ferric oxide. These products were more tightly adhered in the treated troughs as opposed to the looser and more voluminous product formed on the specimens in the untreated trough. Typical specimens from each treatment are shown in Figure 42.



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Table 26. Average mass loss (g) and corrosion rate (mpy) for cast iron in an alternate immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	5.64	3.38	4.31	4.59
Average % Mass Loss	1.95%	1.14%	1.48%	1.56%
Average Corrosion Rate (mpy)	6.66	3.99	5.09	5.42



Figure 42. Great Lakes water, alternate immersion environment, typical cast iron.

Under constant immersion conditions, cast iron in deoxygenated lake water clearly held a corrosion rate advantage over the untreated, chlorinated or chlorine dioxide treated systems. The values, given in Table 27 show a corrosion rate of 0.83 mpy was calculated for cast iron in deoxygenated lake water, a decrease in corrosion rate as compared to untreated lake water, which was 3.01 mpy. The specimens in the remaining treatment systems experienced similar, increased corrosion rates of 3.15 mpy and 3.30 mpy, respectively. Constant immersion prevented hardening and encrustation of the corrosion layer normally seen with intermittent drying of the specimens and common to alternate immersion. The corrosion layer visible in the typical pre-clean photographs in Figure 43 was easily removed.



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Table 27. Average mass loss (g) and corrosion rate (mpy) for cast iron in constant immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	2.55	0.70	2.67	2.80
Average % Mass Loss	0.87%	0.24%	0.91%	0.94%
Average Corrosion Rate (mpy)	3.01	0.83	3.15	3.30

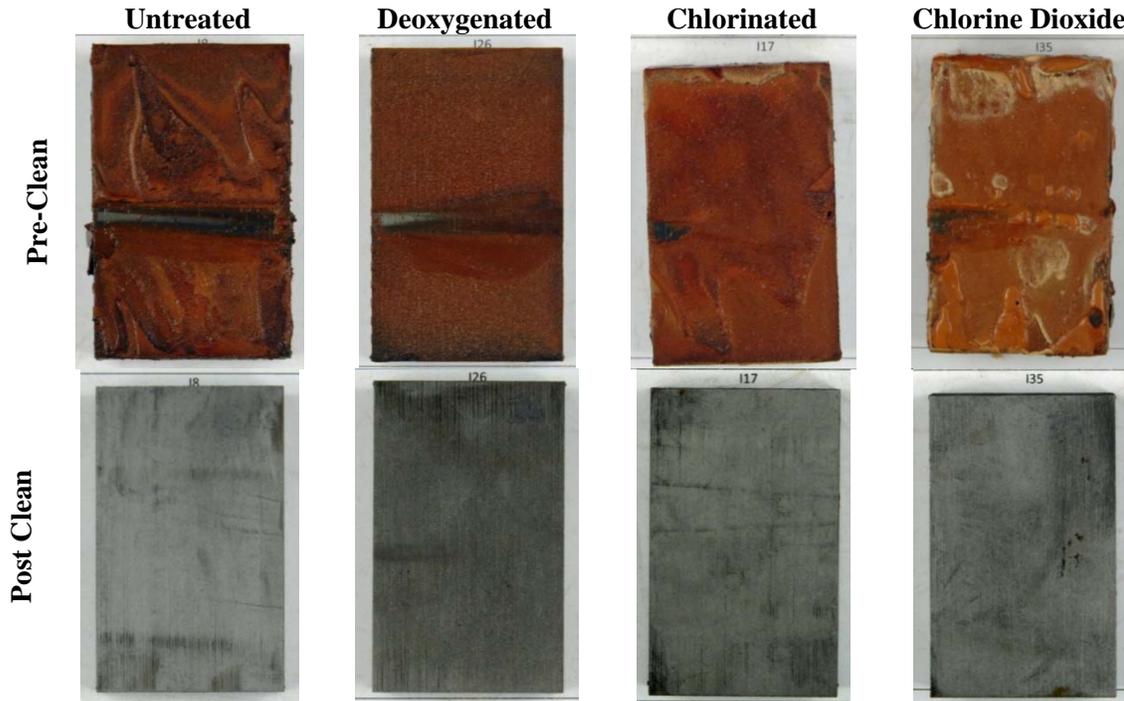


Figure 43. Great Lakes water, constant immersion environment, typical cast iron.

4.6.4 Brass

Corrosion rates calculated for brass exposed to the humid environment of lake water troughs containing the different treatments are shown in Table 28. The corrosion rates ranged from 0.01 mpy to 0.02 mpy, the magnitude and difference of which may be considered negligible. The corrosion sites visible in Figure 44 are most likely from condensate or water dripped on the specimens during fill, drain or documentation procedures.

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Table 28. Average mass loss (g) and corrosion rate (mpy) for brass in a humid lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.02	0.01	0.01	0.02
Average % Mass Loss	0.02%	0.01%	0.01%	0.02%
Average Corrosion Rate (mpy)	0.02	0.01	0.01	0.02

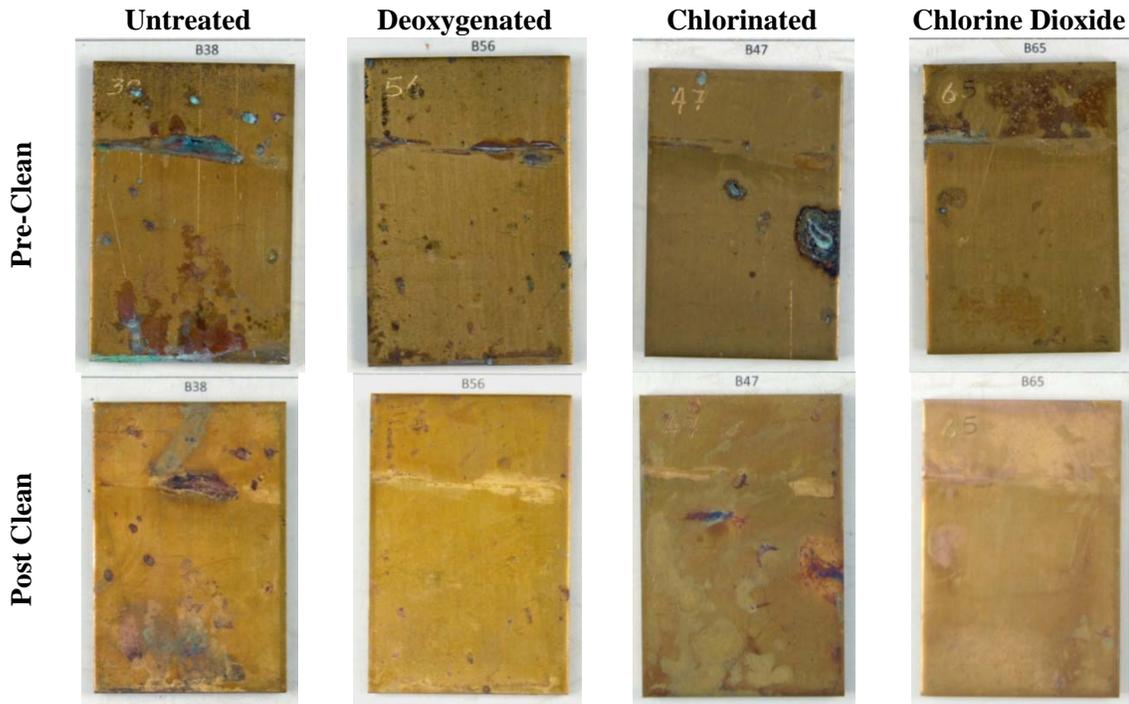


Figure 44. Great Lakes water, humid environment, typical brass.

Brass in the untreated and deoxygenated alternate immersion environments experienced negligible corrosion rates of 0.03 mpy. Corrosion rates in chlorinated and chlorine dioxide treated lake water were low as well; however, the corrosion rates were two and four times as great for these treatments, being 0.07 and 0.12 mpy, respectively and are presented in Table 29. Intermittent chlorine dosing of 2-3 parts per million (ppm) has been known to cause susceptibility of copper to erosion corrosion.^{vii} Additionally Kirmeyer cites increased copper alloy corrosion rates in the presence of chloramines and free chlorine,^{viii} with brass being particularly susceptible as pH decreases.^{viii} Reddish or pink colored areas, typically indicative of dealloying are visible on the specimens exposed to chlorine and chlorine dioxide in Figure 45.

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Table 29. Average mass loss (g) and corrosion rate (mpy) for brass in an alternate immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.03	0.03	0.06	0.10
Average % Mass Loss	0.03%	0.02%	0.06%	0.10%
Average Corrosion Rate (mpy)	0.03	0.03	0.07	0.12

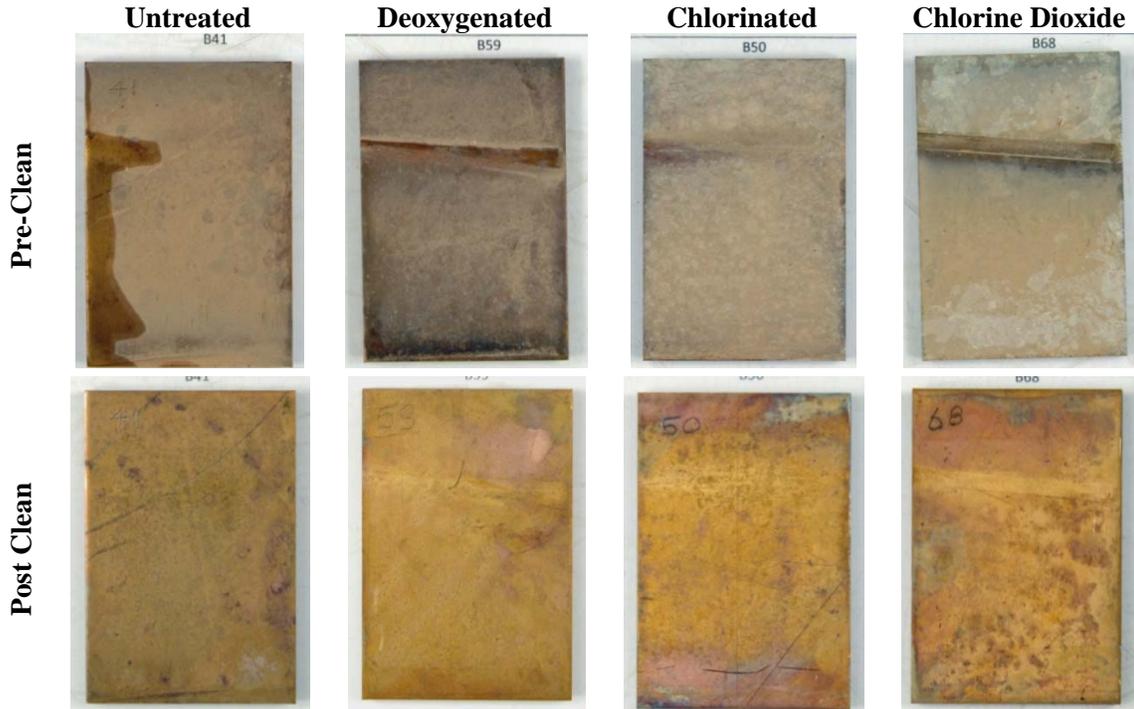


Figure 45. Great Lakes water, alternate immersion environment, typical brass.

The results for brass in a constant immersion lake water environment are nearly identical to the alternate immersion results. Corrosion rates given in Table 30 were a low 0.02 mpy for specimens in the untreated and deoxygenated troughs. The corrosion rate increased three-fold in the chlorinated trough and more than six-fold in the trough treated with chlorine dioxide to rates of 0.06 mpy and 0.13 mpy, respectively. The photographs in Figure 46 show relatively clean brass specimens from the untreated and deoxygenated troughs, but a large area of de-alloying on the specimen exposed to chlorine dioxide treatment.

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Table 30. Average mass loss (g) and corrosion rate (mpy) for brass in constant immersion lake water environment.

	Untreated	Deoxygenation	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.02	0.01	0.06	0.12
Average % Mass Loss	0.01%	0.01%	0.05%	0.11%
Average Corrosion Rate (mpy)	0.02	0.02	0.06	0.13

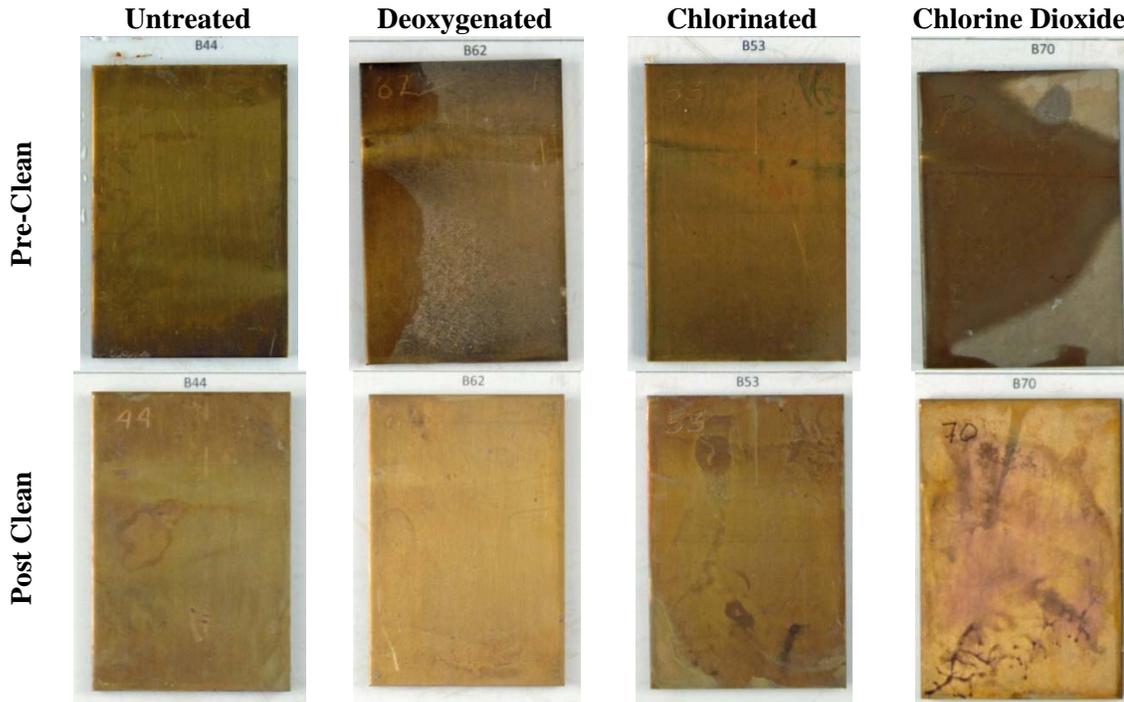


Figure 46. Great Lakes water, constant immersion environment, typical brass.

4.6.5 Copper-Nickel

Corrosion rates for copper-nickel in a humid environment ranged from 0.01 mpy to 0.04 mpy, which may be considered negligible. These values are given in Table 31. Some localized staining was noted near specimen supports on the untreated specimens and those in the trough treated with chlorine dioxide. This staining, can be seen on the pre-cleaned specimens in Figure 47 and was fully removed during specimen cleaning.



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Table 31. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in a humid lake water environment.

Medium	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.02	0.01	0.02	0.04
Average % Mass Loss	0.02%	0.01%	0.02%	0.03%
Average Corrosion Rate (mpy)	0.02	0.01	0.02	0.04



Figure 47. Great Lakes water, humid environment, typical copper-nickel.

Copper-nickel in the untreated and deoxygenated alternate immersion environments experienced negligible corrosion rates of 0.03 mpy and 0.02 mpy, respectively. Corrosion rates in chlorinated and chlorine dioxide treated lake water were low as well; however, the corrosion rates were a minimum of three times as great for these treatments, being 0.06 and 0.11 mpy, respectively. These rates are given in Table 32. Although not as susceptible to chlorine dosing as brass, intermittent dosing clearly had an effect on the copper-nickel alloy as well. The typical photographs in Figure 48 show relatively clean copper-nickel specimens; however, the specimen exposed to chlorine dioxide treatment also exhibits a reddish hue indicative of de-alloying of copper alloys.

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Table 32. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in an alternate immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.02	0.02	0.06	0.11
Average % Mass Loss	0.02%	0.01%	0.05%	0.09%
Average Corrosion Rate (mpy)	0.03	0.02	0.06	0.11

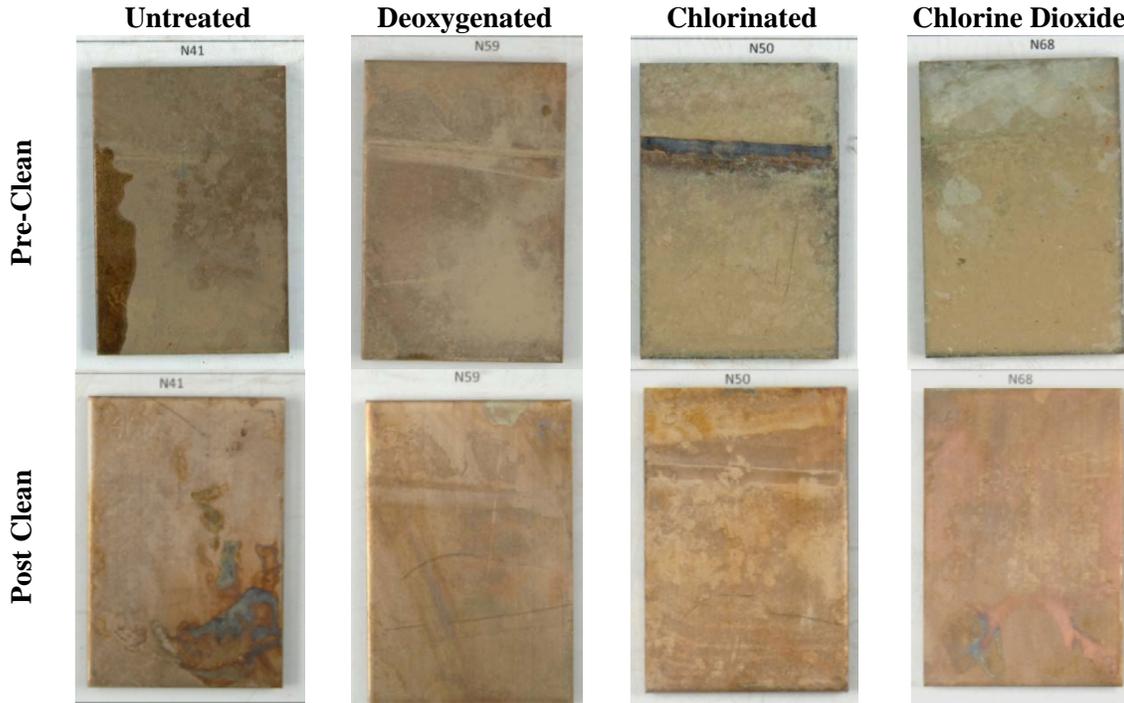


Figure 48. Great Lakes water, alternate immersion environment, typical copper-nickel.

The results for copper-nickel specimens in a constant immersion environment are similar to the alternate immersion results. Corrosion rates given in Table 33 were a low 0.01 mpy for specimens in the untreated and deoxygenated troughs. The corrosion rate more than quadrupled in the chlorinated trough and increased to 0.14 mpy in the trough treated with chlorine dioxide. Similar to the alternate immersion specimens, the typical photographs in Figure 49 show relatively clean copper-nickel specimens; however, the specimen exposed to chlorine dioxide treatment also exhibits a reddish hue common to de-alloying of copper alloys.

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Table 33. Average mass loss (g) and corrosion rate (mpy) for copper-nickel in constant immersion lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Average Mass Loss (g)	0.01	0.01	0.04	0.13
Average % Mass Loss	0.01%	0.00%	0.03%	0.11%
Average Corrosion Rate (mpy)	0.01	0.01	0.04	0.14

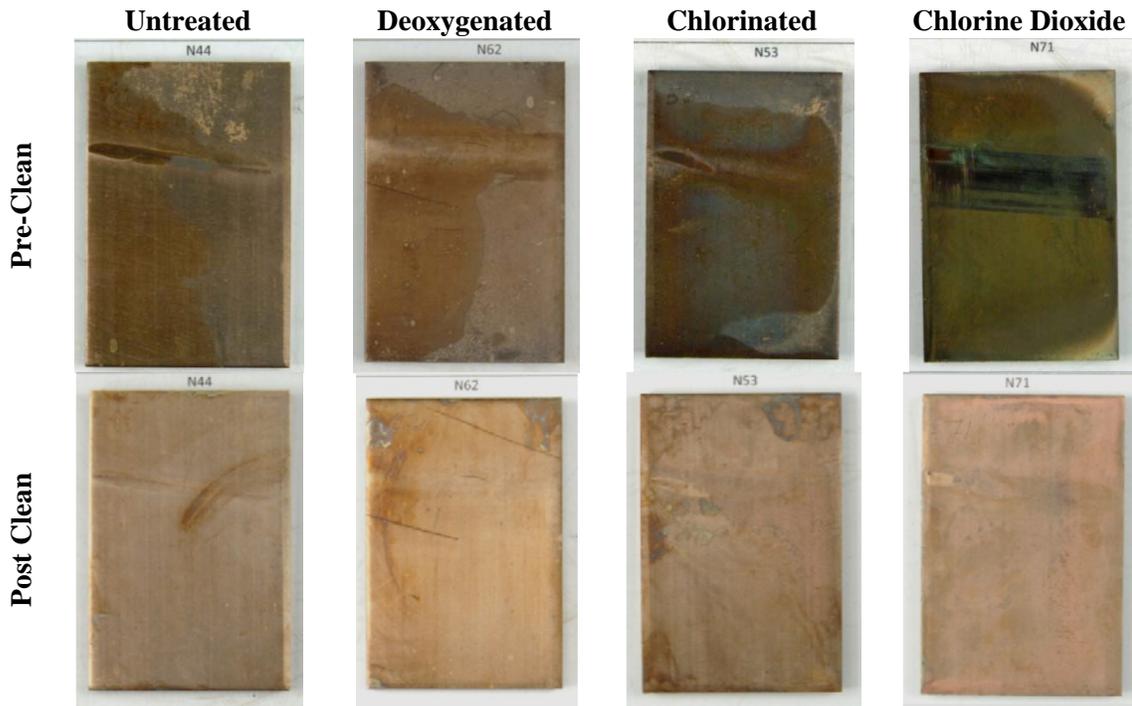


Figure 49. Great Lakes water, constant immersion environment, typical copper-nickel.

4.6.6 Glyon® Gasket

Glyon® gasket material exposed to lake water showed smaller mass changes than did specimens exposed to seawater. The maximum mass difference under any of the lake water treatment-environment combinations tested was mass loss of 2.2 milligrams (mg) in the constant immersion environment, which may be considered negligible as compared to the original mass of the specimens (approximately 13 grams). All humid environment and alternate immersion specimens experienced mass losses of less than 1.0 mg, while the mass losses for the constant immersion specimens ranged from 1.9 mg to 2.2 mg. Mass loss data for the Glyon® gasket material exposed to lake water is given in Table 34. Photographs of typical specimens for each triplicate set are shown in Figure 50. Additionally, no cracking or change in flexibility of the material was noted under any conditions.

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Table 34. Mass loss (mg) and percent mass loss for Glyon® gasket material in a lake water environment.

	Untreated	Deoxygenated	Chlorinated	Chlorine Dioxide
Humid	0.1	-0.9	0.9	0.1
	0.00%	-0.01%	0.01%	0.00%
Alternate Immersion	1.1	0.8	-0.2	0.5
	0.01%	0.01%	0.00%	0.00%
Constant Immersion	2.2	2.1	1.9	2.0
	0.02%	0.02%	0.01%	0.01%

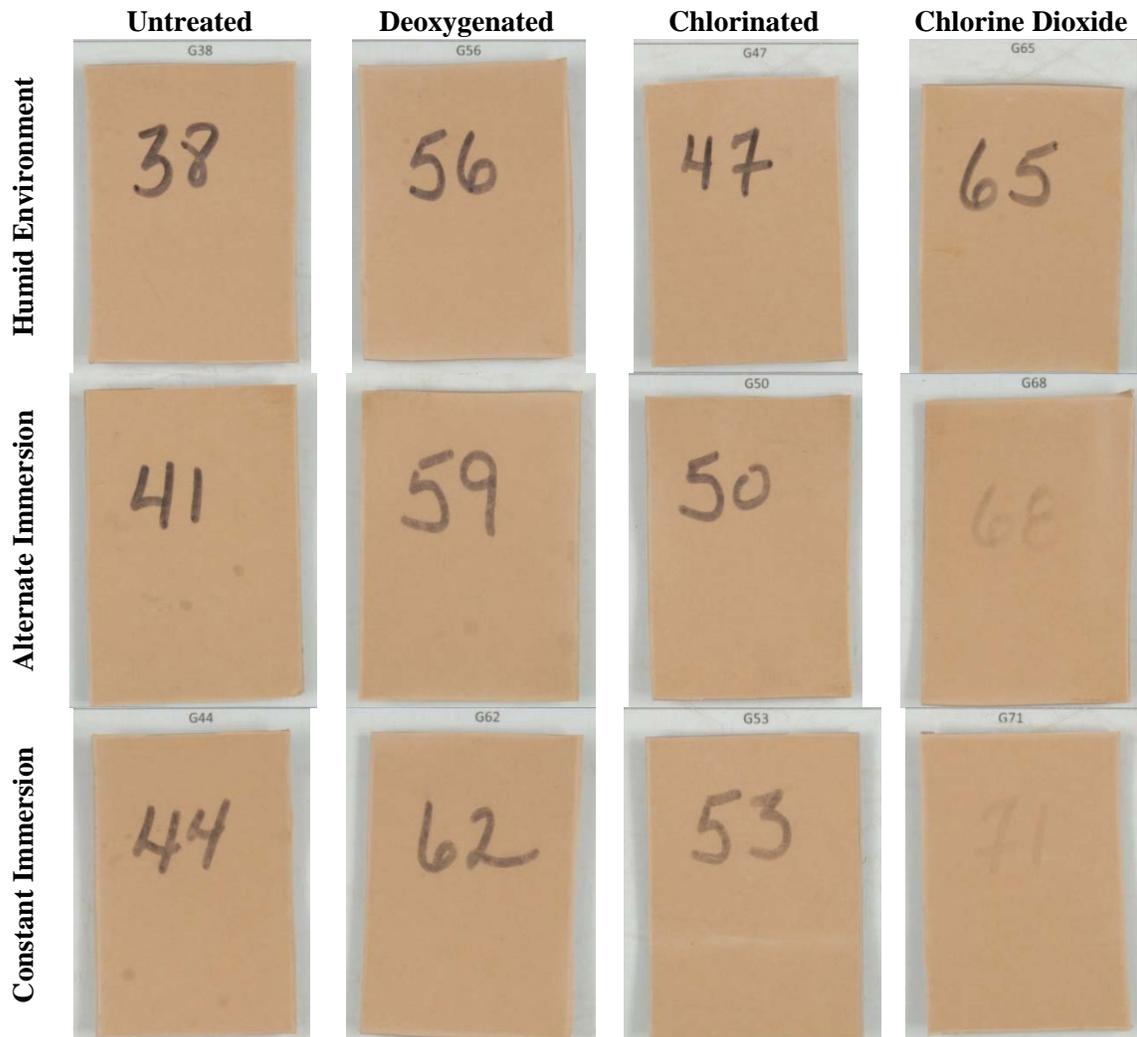


Figure 50. Great Lakes water, typical Glyon® gasket specimens.



5 SUMMARY. COMPARISON BY TREATMENT, CORROSION RATES IN SEAWATER AND GREAT LAKES WATER

A summary of the calculated corrosion rate data from specimens exposed to seawater, treated and untreated, is given in Figure 51 through Figure 53. It can be seen that an active treatment did not always result in the lowest corrosion rate and no single treatment provided the least corrosive environment under all conditions studied. In the case of the humid seawater environment, Figure 51, the lowest corrosion rate for four of the alloys occurred in the untreated trough, but the treatment that resulted in the lowest corrosion rate was chlorination. Chlorine dioxide treatment shows promise in alternate immersion, Figure 52, reducing the corrosion rate of all alloys except brass and in constant immersion Figure 53, reducing the corrosion rate of all alloys.

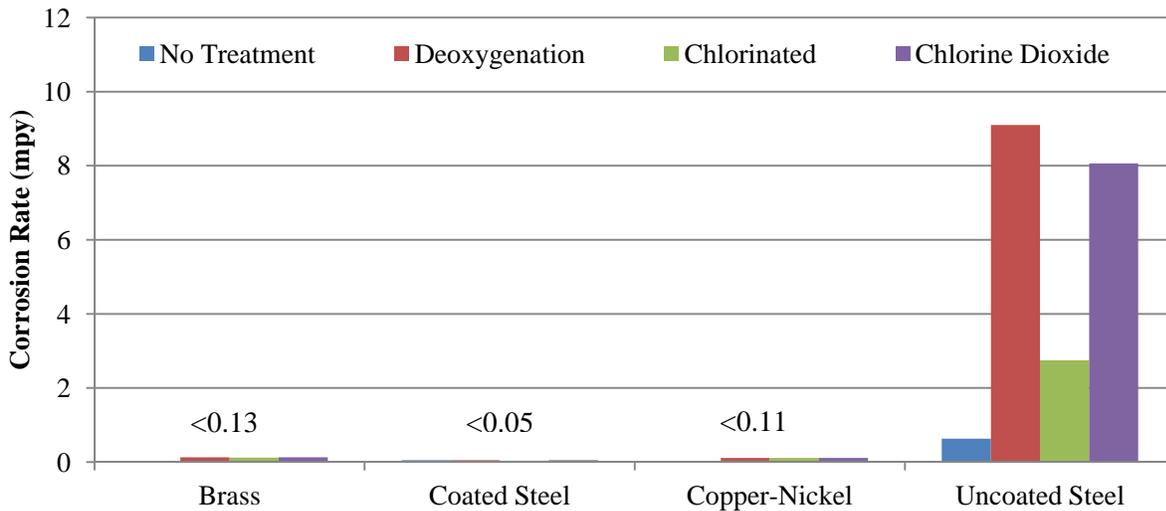


Figure 51. Comparison of corrosion rates in the humid seawater environment.

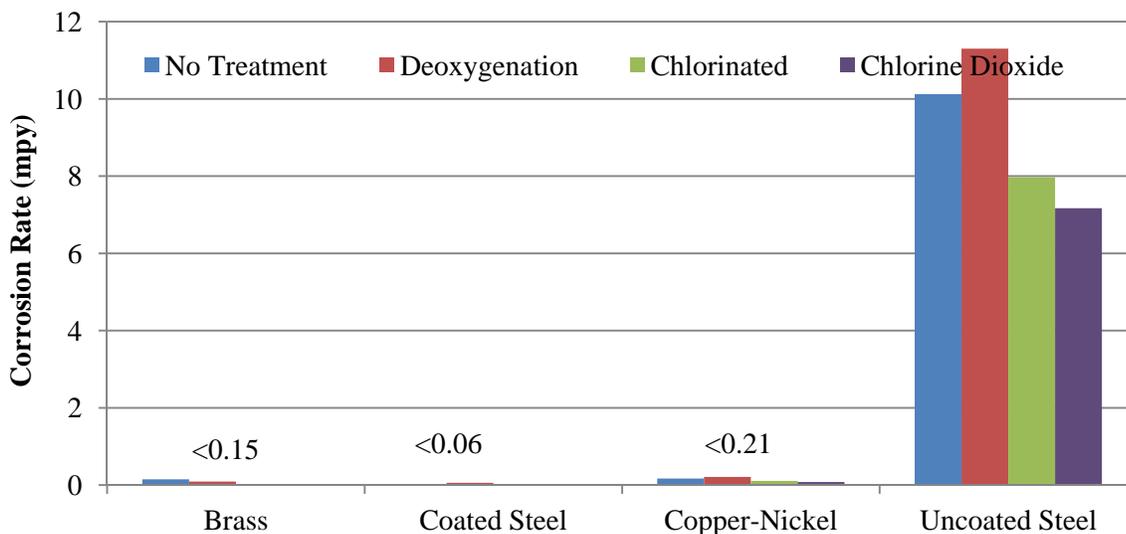


Figure 52. Comparison of corrosion rates in the alternate immersion seawater environment.



Investigation Of Ballast Water Treatment's Effect On Corrosion

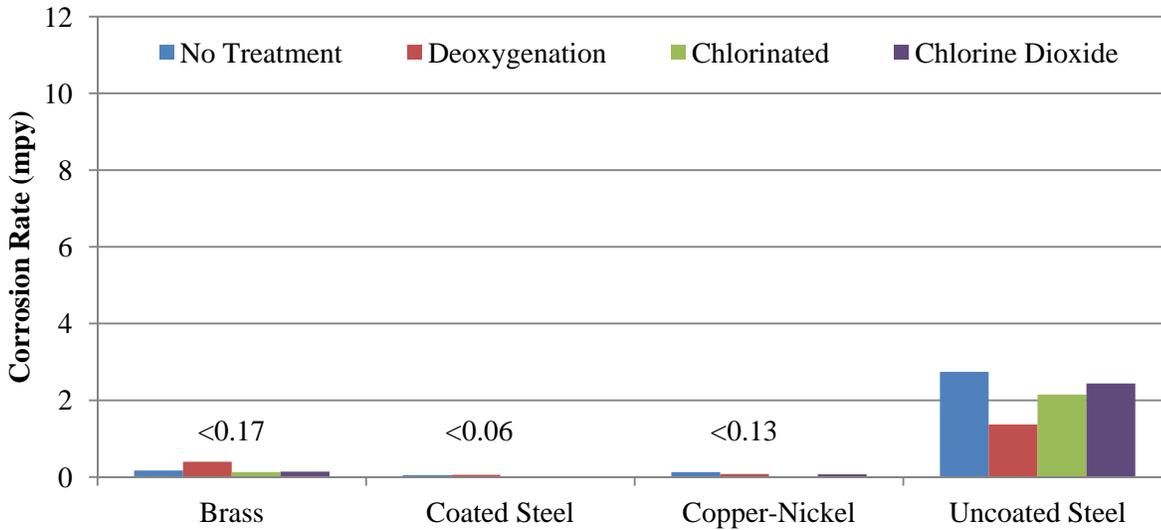


Figure 53. Comparison of corrosion rates in the constant immersion seawater environment.

A similar summary for lake water results is given in Figure 54 through Figure 56, where chlorine dioxide treatment resulted in the highest calculated corrosion rates in ten of fifteen possible material/environment combinations, including the three iron-based alloys in the humid environment (Figure 54) and all five metallic materials in the constant immersion environment, (Figure 56). In the constant immersion environment, deoxygenation proved to have a clear advantage over chlorination or chlorine dioxide treatment. Results for steel specimens were divided between deoxygenation and chlorination. With regard to copper alloys, untreated water, deoxygenation and chlorine dioxide treatment all resulted in negligible corrosion rates in Great Lakes water.

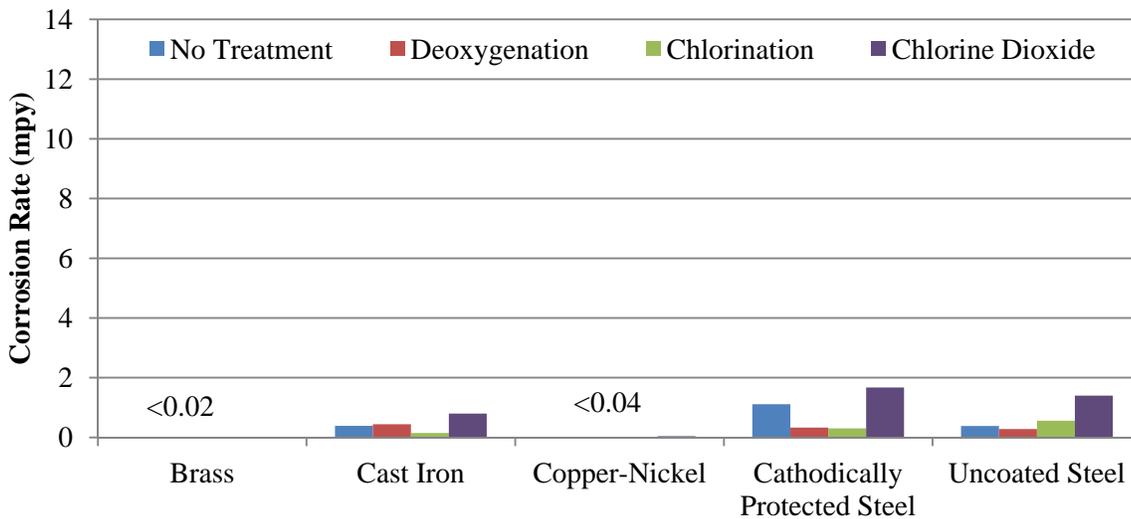


Figure 54. Comparison of corrosion rates in the humid lake water environment.



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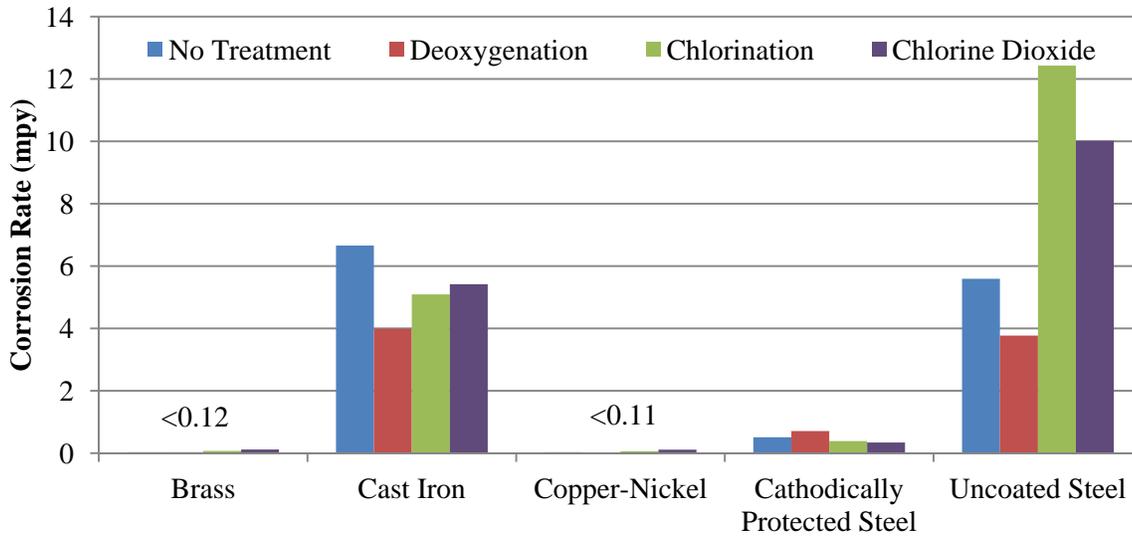


Figure 55. Comparison of corrosion rates in the alternate immersion lake water environment.

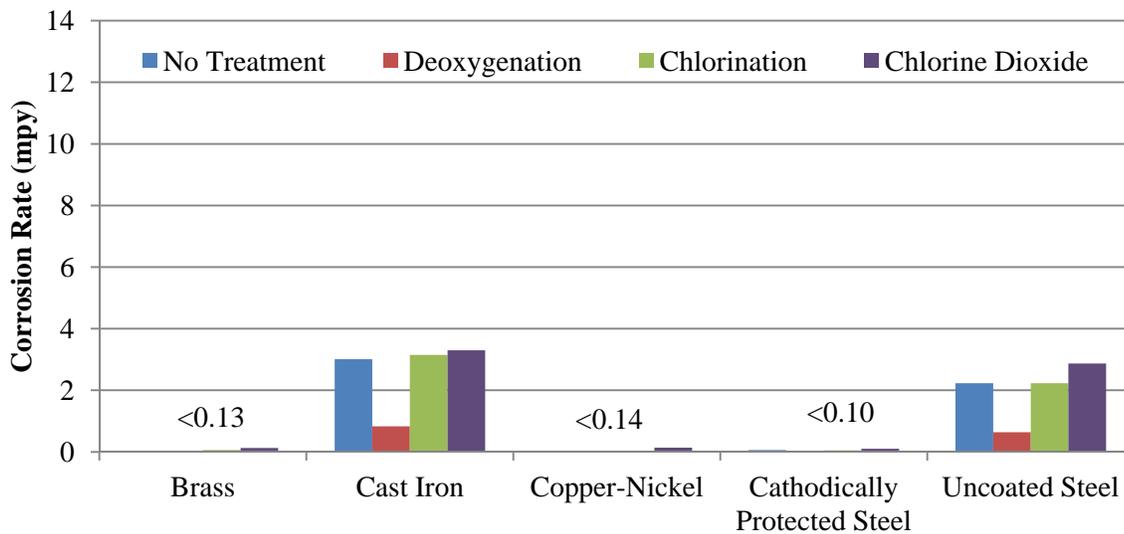


Figure 56. Comparison of corrosion rates in the constant immersion lake water environment.

6 COMPARISON OF THE CORROSION RATE OF MATERIALS UNDER A GIVEN TREATMENT AND ENVIRONMENTAL CONDITION

6.1 Seawater

In the untreated seawater trough, coated steel, brass and copper-nickel all experienced corrosion rates of less than 0.20 mpy, regardless of the exposure condition. In the humid condition, exposed steel experienced surface corrosion equivalent to the rate of 0.63 mpy. In either immersion environment, the corrosion rate of the uncoated steel increased to 10.12 mpy in alternate and 2.74 mpy in constant immersion. This data, which has been previously presented, has been condensed in Table 35, for convenience.

Investigation Of Ballast Water Treatment's Effect On Corrosion

Table 35. Corrosion rates (mpy) for construction materials in seawater.

Material	Treatment	Humid	Alternate Immersion	Constant Immersion
Brass	Untreated	0.01	0.15	0.17
Coated Steel		0.05	0.03	0.05
Copper-Nickel		0.03	0.17	0.13
Uncoated Steel		0.63	10.12	2.74
Brass	Deoxygenation	0.13	0.21	0.40
Coated Steel		0.05	0.06	0.08
Copper-Nickel		0.11	0.09	0.06
Uncoated Steel		9.10	11.30	0.96
Brass	Chlorinated	0.12	0.18	0.28
Coated Steel		0.04	0.03	0.02
Copper-Nickel		0.11	0.11	0.13
Uncoated Steel		2.75	7.97	2.15
Brass	Chlorine Dioxide	0.13	0.18	0.14
Coated Steel		0.05	0.01	0.00
Copper-Nickel		0.11	0.08	0.07
Uncoated Steel		8.06	7.17	2.44

Coated steel, copper-nickel and brass were also the top performers in deoxygenated seawater. Calculated corrosion rates for brass increased as the exposure to seawater increased, but were still below 0.40 mpy. Deoxygenation appeared to have the reverse effect on copper-nickel, with corrosion rates decreasing with increased exposure to seawater. Uncoated steel experienced the greatest corrosion rates at 9.10 mpy and 11.30 mpy in the humid and alternate immersion deoxygenated environments, respectively. This rate was greatly reduced to 0.96 mpy in the constant immersion condition.

The coated steel, brass and copper-nickel performance trend continued for specimens in the humid environment above chlorinated and chlorine dioxide treated seawater, with a maximum corrosion rate of 0.28 mpy for brass under chlorinated constant immersion conditions. In the chlorinated environment, the corrosion rates of uncoated steel were similar in the humid and constant immersion environment, but experienced an increase to 7.97 mpy in alternate immersion. Alternate and constant immersion rates for uncoated steel in the chlorinated or chlorine dioxide treated seawater were similar, however, uncoated steel in the humid chlorine dioxide environment experienced a corrosion rate of 8.06 mpy.

6.2 Great Lakes Water

The performance of brass and copper-nickel were nearly identical in all lake water environments. These materials were also the most corrosion resistant of the materials tested in all environments with the exception of constant immersion in chlorine dioxide treated lake water, where cathodically protected steel held a slight edge. In all environments except chlorine dioxide treated alternate and constant immersion, the calculated corrosion rate of these materials was below 0.10 mpy. The rate in immersion environments with chlorine dioxide rose to a maximum of 0.14 mpy. Corrosion rates in Great Lakes water has been condensed in Table 36.

Investigation Of Ballast Water Treatment's Effect On Corrosion

Table 36. Corrosion rates (mpy) for construction materials in Great Lakes water.

Material	Treatment	Humid	Alternate Immersion	Constant Immersion
Brass	Untreated	0.02	0.03	0.02
Cast Iron		0.39	6.66	3.01
Copper-Nickel		0.02	0.03	0.01
Cathodically Protected Steel		1.11	0.51	0.06
Uncoated Steel		0.38	5.59	2.23
Brass	Deoxygenation	0.01	0.03	0.02
Cast Iron		0.44	3.99	0.83
Copper-Nickel		0.01	0.02	0.01
Cathodically Protected Steel		0.33	0.71	0.04
Uncoated Steel		0.28	3.77	0.64
Brass	Chlorinated	0.01	0.07	0.06
Cast Iron		0.15	5.09	3.15
Copper-Nickel		0.02	0.06	0.04
Cathodically Protected Steel		0.30	0.39	0.05
Uncoated Steel		0.56	12.43	2.23
Brass	Chlorine Dioxide	0.02	0.12	0.13
Cast Iron		0.80	5.42	3.30
Copper-Nickel		0.04	0.11	0.14
Cathodically Protected Steel		1.67	0.34	0.10
Uncoated Steel		1.40	10.02	2.87

Cathodic protection provided no advantage over unprotected steel or cast iron in the humid environment, which is not unexpected, as little protection is afforded without a complete cathodic protection circuit. Cathodically protected steel specimens experienced the highest corrosion rates of 1.11 mpy and 1.67 mpy in the atmosphere above untreated and chlorine dioxide treated water, respectively. In the alternate immersion environment, cathodic protection reduced the corrosion rate of uncoated steel by as much as 12.04 mpy (chlorinated trough). Corrosion rate reductions ranged from 0.60 mpy (deoxygenated) to 2.77 mpy (chlorine dioxide treatment). In either alternate immersion or constant immersion, uncoated, unprotected steel and cast iron behaved similarly and experienced the highest corrosion rates in the respective troughs.

7 CONCLUSIONS

7.1 Seawater Exposure

7.1.1 Uncoated Steel

- The corrosion rate ranking for uncoated steel in the humid environment, from the most corrosive to least corrosive is deoxygenated, chlorine dioxide, chlorinated, untreated.

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- The corrosion rate ranking for uncoated steel in the alternate immersion environment, from the most corrosive to least corrosive is deoxygenated, untreated, chlorinated, chlorine dioxide.
- The corrosion rate ranking for uncoated steel in the constant immersion environment, from the most corrosive to least corrosive is untreated, chlorine dioxide, chlorinated, deoxygenated.

7.1.2 Coated Steel

- Coated steel experienced negligible mass loss and subsequent corrosion rates regardless of treatment or immersion condition. The corrosion rates for coated steel were all below 0.1 mpy.

7.1.3 Coated and Scribed Steel

- In the humid environment, corrosion ranking of coated and scribed steel from the most corrosive to the least corrosive, based on visual assessment is chlorine dioxide, deoxygenation, untreated, chlorinated.
- In the alternate immersion environment, corrosion ranking of coated and scribed steel from the most corrosive to the least corrosive, based on visual assessment is deoxygenation, chlorine dioxide, untreated, chlorinated.
- In the alternate immersion environment, corrosion developed at the scribe regardless of treatment. There was no coating disbondment or undercutting noted at the scribe on any of the scribed steel specimens.
- In the constant immersion environment, corrosion ranking of coated and scribed steel from the most corrosive to the least corrosive, based on visual assessment is untreated, deoxygenation, chlorine dioxide, chlorinated.

7.1.4 Cathodically Protected Steel

- In the humid environment, coated, scribed and cathodically protected steel specimens responded in a manner similar to the scribed, unprotected specimens and were similar in appearance. Greater amounts of corrosion were noted on specimens in the atmosphere above deoxygenated and chlorine dioxide treated seawater.
- In the humid environment, corrosion ranking of cathodically protected coated and scribed steel from the most corrosive to the least corrosive, based on visual assessment is chlorine dioxide, deoxygenation, untreated, chlorinated.
- In the alternate immersion environment, scribed and cathodically protected steel specimens developed protective calcareous deposits; however, the nature of alternate immersion allowed some corrosion to form prior to the deposits becoming fully developed.
- In the alternate immersion environment, corrosion ranking of cathodically protected coated and scribed steel from the most corrosive to the least corrosive, based on visual assessment is difficult to determine as all specimens have a similar appearance.
- In the constant immersion environment, fully developed calcareous deposits were formed on all specimens regardless of treatment. No corrosion was noted in the scribe area.

7.1.5 Brass

- In the humid environment, brass specimens experienced the lowest corrosion rates in the atmosphere above untreated seawater. The corrosion rate of brass increased in all treated troughs. All corrosion rates in the humid environment were less than 0.15 mpy.
- The corrosion rate ranking for brass in the humid environment, from the most corrosive to least corrosive is deoxygenated and chlorine dioxide (equal), chlorinated, untreated.

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- In the alternate immersion environment, the differences between corrosion rates of brass specimens were negligible. Rates were low and ranged from 0.15 mpy in untreated seawater to 0.21 mpy in deoxygenated seawater.
- The corrosion rate ranking for brass in the alternate immersion environment, from the most corrosive to least corrosive is deoxygenated, chlorinated and chlorine dioxide (equal), untreated.
- In the constant immersion environment, brass specimens in chlorine dioxide treated seawater experienced the lower corrosion rates (0.14 mpy) than in untreated seawater (0.17 mpy) Corrosion rates increased in chlorinated seawater (0.28 mpy) and deoxygenated seawater (0.40 mpy).
- The corrosion rate ranking for brass in the constant immersion environment, from the most corrosive to least corrosive is deoxygenated, chlorinated, untreated, chlorine dioxide.

7.1.6 Copper-Nickel

- In the humid environment, copper-nickel specimens experienced the lowest corrosion rates in the atmosphere above untreated water. The corrosion rate of copper-nickel increased in all treated troughs. All corrosion rates in the humid environment were less than 0.12 mpy.
- The corrosion rate ranking for copper-nickel in the humid environment, from the most corrosive to least corrosive is deoxygenated/chlorine dioxide/chlorinated (all equal), untreated.
- In the alternate immersion environment, the differences in corrosion rates between the different treatments were negligible. Rates were low and ranged from 0.08 mpy in chlorine dioxide treated seawater to 0.17 mpy in untreated seawater.
- The corrosion rate ranking for copper-nickel in the alternate immersion environment, from the most corrosive to least corrosive is untreated, chlorinated, deoxygenated, chlorine dioxide.
- In the constant immersion environment, the differences between corrosion rates of copper-nickel specimens were negligible. Rates were low and ranged from 0.06 mpy in deoxygenated seawater to 0.13 mpy in untreated and chlorinated seawater. The highest corrosion rate was experienced by copper-nickel specimens in the untreated and chlorinated troughs.
- The corrosion rate ranking for copper-nickel in the constant immersion environment, from the most corrosive to least corrosive is chlorinated and untreated (equal) chlorine dioxide, deoxygenated.

7.1.7 Glyon

- In seawater, mass changes in Glyon[®] gasket material exposed to any of the treatments in any exposure environment were negligible.
- No deterioration of the Glyon[®] gasket material was noted under any condition studied.

7.2 Great Lakes Water Exposure

7.2.1 Uncoated Steel

- The corrosion rate ranking for uncoated steel in the humid environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated, deoxygenated.
- The corrosion rate ranking for uncoated steel in the alternate immersion environment, from the most corrosive to least corrosive is chlorinated, chlorine dioxide, untreated, deoxygenated.
- The corrosion rate ranking for uncoated steel in the constant immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated and untreated (rates equal), deoxygenated.



7.2.2 Cathodically Protected Steel

- In the humid environment, deoxygenation and chlorinated decreased the corrosion rate of cathodically protected steel while chlorine dioxide treatment increased the corrosion rate.
- The corrosion rate ranking for uncoated, cathodically protected steel in the humid environment, from the most corrosive to least corrosive is chlorine dioxide, untreated, deoxygenated, chlorinated.
- In the alternate immersion environment, cathodically protected steel experienced increased corrosion rates in chlorinated and deoxygenated treated troughs. Corrosion rates of cathodically protected steel were reduced in chlorinated and chlorine dioxide treated troughs.
- The corrosion rate ranking for uncoated, cathodically protected steel in the alternate immersion environment, from the most corrosive to least corrosive is deoxygenated, untreated, chlorinated, chlorine dioxide.
- In the constant immersion environment, the corrosion rates of cathodically protected steel were less than 0.10 mpy for all treatments studied. The differences between treatments are considered negligible.
- The corrosion rate ranking for uncoated, cathodically protected steel in the constant immersion environment, from the most corrosive to least corrosive is chlorine dioxide, untreated, chlorinated, deoxygenated.

7.2.3 Cast Iron

- The corrosion rate ranking for cast iron in the humid environment, from the most corrosive to least corrosive is chlorine dioxide, deoxygenated, untreated, chlorinated. All corrosion rates were below 1.0 mpy.
- The corrosion rate ranking for cast iron in the alternate immersion environment, from the most corrosive to least corrosive is untreated, chlorine dioxide, chlorinated, deoxygenated.
- The corrosion rate ranking for cast iron in the constant immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated, deoxygenated.

7.2.4 Brass

- In the humid environment, brass specimens experienced negligible corrosion rates. All corrosion rates in the humid environment were less than 0.03 mpy.
- The corrosion rate ranking for brass in the alternate immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated/deoxygenated (rates equal). Corrosion rates ranged from 0.03 mpy for untreated and deoxygenated waters to 0.12 mpy for waters containing chlorine dioxide.
- The corrosion rate ranking for brass in the constant immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated/deoxygenated (rates equal). These rates were less than 0.14 mpy.

7.2.5 Copper-Nickel

- The corrosion rate ranking for copper-nickel in the humid environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated and untreated (equal), deoxygenated. Rates were low and ranged from 0.01 mpy in deoxygenated water to 0.04 mpy in chlorine dioxide treated water.
- The corrosion rate ranking for copper-nickel in the alternate immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated, deoxygenated. Corrosion rates ranged from 0.02 mpy in deoxygenated water to 0.11 mpy in chlorine dioxide treated water.



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- The corrosion rate ranking for copper-nickel in the constant immersion environment, from the most corrosive to least corrosive is chlorine dioxide, chlorinated, untreated/deoxygenated (rates equal). Corrosion rates ranged from 0.01 mpy in untreated and deoxygenated water to 0.14 mpy in chlorine dioxide treated water.

7.2.6 Glyon[®]

- In Great Lakes water, mass changes in Glyon[®] gasket material exposed to any of the treatments in a humid or alternate immersion exposure environment are negligible and may be the result of tightly adhered sediment.
- No deterioration of the Glyon[®] gasket material was noted under any lake water condition studied.

8 REFERENCES

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