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THE CORROSION EFFECT OF OZONATED SEAWATER SOLUTION ON TITANIUM IN POLYMER GENERATED CREVICE ENVIRONMENTS

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THE CORROSION EFFECT OF OZONATED SEAWATER SOLUTION ON TITANIUM IN POLYMER GENERATED CREVICE ENVIRONMENTS

by

Susan Y. Leveillee

A Thesis submitted to the Graduate
Faculty of Rensselaer Polytechnic Institute
in Partial Fulfillment of the Requirements for the Degree of

MASTER of SCIENCE

Approved:

____

David J. Duquette
Thesis Advisor

Rensselaer Polytechnic Institute
Troy, New York

November 1997
(For Graduation December 1997)

Dedicated to my nephews and niece
Lucas M., Nicholas J., and Casey L. Leveillee
Our Future

Dedicated to my parents,
Ms Rita C. Blanchette and Mr. Charles M. Leveillee
My Grandparents,
Anita & Herve Leveillee and Beatrice & Ernest Blanchette
and
My Family and Friends
for Their Support, Patience and Encouragement Through My Trials
and Successes

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ABSTRACT

Two different tests were designed to evaluate the reaction of various polymers and grade-2 titanium in ozonated seawater in conjunction with a comparative analysis in an aerated seawater solution. The first was a weight loss test measuring the weight change of Polyvinyl chloride (PVC), Polyethylene and Teflon™ in both ozonated and aerated artificial seawater baths. The second test was designed to induce crevice corrosion on the titanium test samples using various crevice generating materials in both ozonated and aerated solutions. The materials used to create the crevices were grade-2 titanium washers, PVC, Polyethylene, Saran and Teflon™.

The weight loss test showed that all three polymers lost weight in the ozonated bath. On average, under ozonated conditions, PVC lost approximately 0.6 % of its original mass, polyethylene 1.4%, and Teflon™ 0.03% whereas, the results in the aerated tank were mixed. PVC actually gained about 0.05% of its original weight, the polyethylene showed a 0.03% weight loss, and the Teflon™ weight loss was the same as in the ozonated solution (0.03%). The PVC weight loss samples also demonstrated a whitening effect.

The results of the titanium washer crevice test provided no indication of corrosion or surface discoloration in either the ozonated or aerated solutions. Energy dispersive spectrometry (EDS) analysis found no fluorine, chlorine or other corrosion product. The PVC samples in the aerated bath also showed no signs of corrosion, but the PVC samples in the ozonated tank had light brown rings of surface discoloration. One of the ozonated PVC samples did show evidence of chlorine in the corrosion product. The outer circumference of the ozonated PVC washers exhibited the same type bleaching effect as in the weight loss samples, but the whitening of these samples was more pronounced. The polyethylene samples under aeration showed no discoloration or presence of fluorine or chlorine. The polyethylene crevice samples in the ozonated solution all exhibited the distinct brilliant blue color of titanium oxide. Fluorine was found in the corrosion product on only one of the samples. Chlorine was found on the surface of one of the other corrosion coupons.

The results of the Teflon™ crevice samples substantiated the previous Rensselaer study. Samples in the ozonated seawater bath developed crevice corrosion on the surfaces underneath and in the immediate area of the Teflon™ washers. EDS analysis of these areas identified fluorine in the corrosion product. In addition, the Teflon™ crevice samples in the aerated seawater solution demonstrated signs of microscopic crevice corrosion and presence of chlorine as well as fluorine on the effected surfaces.

PART 1
INTRODUCTION

Unexpected crevice corrosion data were generated by, Brown, Wyllie and Duquette during recent corrosion studies at Rensselaer Polytechnic Institute.[2] The environment for these results consisted of an ozonated, artificial seawater solution at room temperature. Crevices were created using crenelated Teflon™ washers and a commercial grade-2 titanium corrosion coupon. These results warranted further investigation. Thus, tests for this thesis were designed to validate or if necessary disprove the results of the Brown, Wyllie and Duquette study. The previous results suggested that grade-2 titanium, normally inert in an ozone, seawater environment, degrades by the mechanism of crevice corrosion at room temperature using Teflon™ to generate the crevices. In addition, fluorine was found in the corrosion product. It is the objective of this thesis and supporting research to substantiate or refute the titanium crevice corrosion results of this 1996 study and postulate possible mechanisms to explain this phenomenon.

Recorded references to ozone are recorded as far back as Greek literature. In the Odyssey, book XII, verse 417, Zeus sends a thunderbolt, "full of sulphurous odor" to strike a ship.[1] Since its initial discovery using electrolysis, by Schonbein in 1840 and its recognition as a water disinfectant in 1886 by de Meritens, ozone has had limited success as a drinking water treatment. At the turn of the century ozone plants were constructed at a steady rate in many parts of the world to disinfect and improve the taste and odor of drinking water. After World War I, except for Switzerland, Germany and France in particular, most countries shifted away from the use of ozone. The majority of treatment facilities built after that time processed water using chlorine, the new and relatively inexpensive chemical discovered during World War I poison gasses experiments.[1, 21]

After World War II there was a resurgence of ozone technology for public water treatment. This resurgence has been fueled by improved efficiency of ozone generation and the concerns over the environmental impact of chlorine. There is much research available on the behavior and effects of ozone on our environment and its toxicity to humans and other life. However, published data on its effect to materials and equipment are rather scarce. In an effort to better understand ozone's effects on engineering and structural materials, research in this area is current and ongoing.

Technological advances have provided our society with numerous types of new materials. Polymers, ceramics, composites, superalloys, and micro-materials are just a few of the more recent developments. These advances have outdated the conventional definition of corrosion, the destructive result of chemical reaction between a metal or metal alloy and its environment. The more general definition of corrosion, the "destruction or deterioration of a material because of reaction with its environment," [4] is preferred. This broader interpretation is more pertinent in the context of this corrosion study, since experiments point to a mechanism of Teflon™ degradation or "corrosion" which initiates and/or propagates the crevice corrosion of titanium in seawater.

PART 2
HISTORICAL REVIEW

2.1 Seawater Chemistry and Biofouling

There are many variables that determine the extent of corrosion in seawater, which is slightly alkaline at a pH of 8. The NaCl salt concentration is an important factor contributing to general corrosion. At higher levels of dissolved salt, there is a decrease in the solubility of dissolved oxygen and the corrosion rate decreases.[3]

Seawater and its reactions are highly complex. Table 2.1 lists the ionic species of seawater. With the exceptions of biofouling (Section 2.1) and ozone reactivity (Section 2.2) this paper will not delve into specific seawater considerations. In order to appreciate the complexity of issues associated with the study of seawater corrosion, a general understanding of the seawater system is required.

Table 2.1 Ionic Composition of Seawater

ION	mg/L or PPM
Chloride, Cl^-	19000
Sulfate, SO_4^{2-}	2700
Bicarbonate, HCO_3^-	140
Bromide, Br^-	65
Fluoride, F^-	1
Boric acid, H_3BO_3	26
Sodium, NA^+	10550
Magnesium, Mg^{2+}	1300
Calcium, Ca^{2+}	400
Potassium, K^+	380
Strontium, Sr^{2+}	13

The American Society of Testing and Measurements (ASTM) approved Bio-Crystals™ Marinemix solutions were used to simulate natural seawater conditions. This artificial seawater is an excellent substitute in laboratory experimentation. Since many factors determine corrosion rates and the extent of damage, other considerations, beyond the test solution, must be briefly mentioned.

As previously discussed, the concentration of salts dissolved in solution play an integral role in the corrosive medium.[3,4] Two other key variables are solution temperature[3,4] and the concentration of dissolved, accessible oxygen[3,4] or in this situation, ozone. Other pertinent considerations are the concentration of ionic species, including the minor ones[3,4]; the presence of biological organisms[3,4]; material surface conditions; extent of alloying; size, geometry and proximity to other objects; the velocity of solution exposed to the material surface[4]; and the seawater depth, as demonstrated by Figure 2.1.[3]

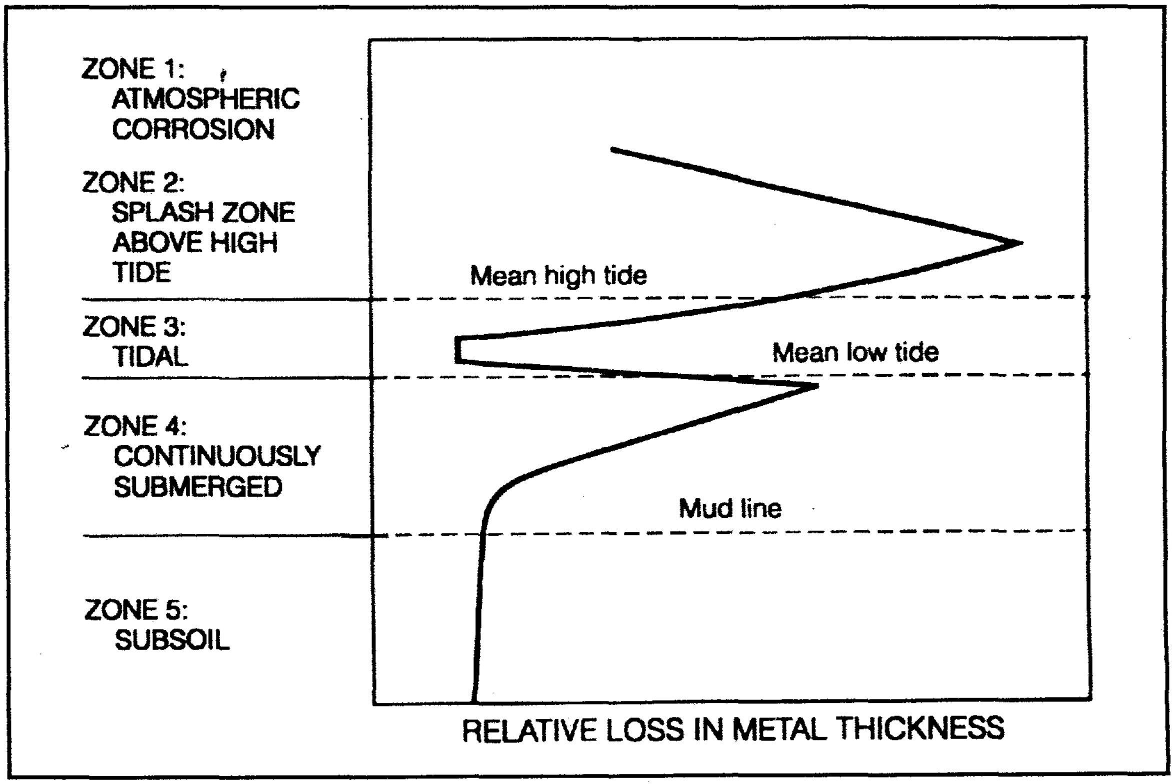


Figure 2.1 Effect of Seawater Depth on the Corrosion of Steel

The presence of biological organisms and their biological and chemical interactions in seawater, commonly referred to as biofouling, present unique challenges to corrosion engineers. Corrosion influencing aquatic life forms can range from micro to macroscopic. Microbiologically influenced corrosion (MIC) is particularly relevant for carbon, stainless steel, copper and aluminum under the conditions of stagnant, continuous contact seawater with a pH range of 4 to 9 and temperatures between 10° to 50° C.[3] Problems occur from the biological wastes and secretions of these organisms.

Examples and conditions for MIC are as varied as the number of organisms, environments and materials of interest. Iron and carbon steels are very susceptible to anaerobic bacteria (not requiring the presence of oxygen for growth), which reduce the level of sulfate. This effect produces corrosive hydrogen sulfide within the water.[3] Many of the aerobic bacteria secrete a biofouling slime used by the bacteria to improve its environment for enhanced growth. This slime is not desirable in water cooled components and piping. Besides its physical disruption of a working system, slime is responsible for affecting the chemistry of a relatively closed system, usually leading to increased corrosion. One final example of microbiological influenced corrosion is in stainless steels. When chlorine is present, aerobically produced biofilms can cause an increase in the corrosion potential above the critical potential for pitting. Pitting and crevice corrosion can propagate as the interior of the pit or crevice becomes anodic to the remaining material.[3]

Macrofouling, occurs when barnacles, mollusks and other large organisms, attach themselves to immersed structures. This can cause similar corrosion problems as with the microscopic bacteria. They can produce corrosive by-products, thereby creating an environment supportive of crevice corrosion and pitting. They also provide anaerobic, sulfate-reducing bacteria an environment to thrive and further propagate the corrosive environment. Macrofouling can also cause restriction in piping and increase the drag of ship hulls.[3]

The main reason for the use of defouling agents such as chlorine, ozone, antifouling paints and various cleaning methods, is to reduce and eliminate the detrimental effects of biofouling. Each method of defouling must be analyzed, under the appropriate service conditions to determine its ultimate effect on the component materials. Biofouling agents can sometimes be beneficial, protecting a material system. Under certain conditions, for specific materials, a thick, uniform biofouling surface forms. This film limits access to the surface by dissolved oxygen, reducing the amount of corrosion.

2.2 Ozone Chemistry and Reactions in Seawater

Since its discovery as a disinfectant and biofouling agent in 1886, ozone has had limited acceptance in the treatment of the world's water supply. France has lead the way in the use of ozone to treat its public water. With environmental concerns an important issue in recent years, ozone is increasingly being investigated as a replacement for chlorine applications. Ozone's highly reactive nature makes it one of the strongest oxidizers used in water purification. There are many unanswered questions concerning ozone's effect on equipment and components designed to perform in a chlorinated environment. Research to answer these concerns is in its infancy and will most certainly continue well into the next millennium.

The most widely used method of ozone production for water treatment is by corona discharge in dry process air containing oxygen.[1] During ozone generation electrical microdischarges, each lasting only several nanoseconds, produce current densities of 100 to 1000 A/cm^2. These microdischarges last 2.5 to 3 times longer in air than in oxygen. There are two other methods of ozone generation. The photochemical process, first reported in 1900 by Lenard, generates ozone from oxygen exposed to ultraviolet (UV) light at a wave length of 140-190 nm. The second method, a radiochemical process, utilizes high-energy radioactive sources emitting β, γ, or neutrons to form ozone from oxygen.

Several factors influence the solubility of ozone in water; e.g., temperature, pH, and ionic strength. Ozone has a theoretical solubility 10 times greater than that of oxygen in pure water, however, it is empirically closer to 1 - 1.5 times that of oxygen in solutions other than pure water.[16] Ozone demand in seawater solution affects the solubility of ozone and is a major factor contributing to the theoretical discrepancy.[16] Ozone demand, involving ozone-depleting impurities and ionic species in solution, must first be satisfied before ozone can be available for water purification and defouling.

The following is a synopsis of ozone chemistry and reactions in seawater as presented in a March 1996 report by Wyllie, Brown and Duquette.[15] Table 2.2 provides a comparative analysis of the reduction potentials of oxidants present in ozonated seawater, in the standard state and at nominal conditions.

Table 2.2 Reduction Potentials of Oxidants Present in Ozonated Seawater

Redox Couple	e^O (V_{SHE})	Nominal Conditions in Artificial Seawater, pH 8.2	e (V_{SHE}) at Nominal Conditions
O_3/O_2	2.08	Ozonated, $p(O_3) = 0.024$ atm	1.55
$HOCl/Cl^-$	1.48	Chlorinated, [HOCl] = 25 mg/l	1.15
$HOBr/Br^-$	1.33	Brominated, [HOBr] = 25 mg/l	1.08
O_2/OH^-	1.23	Oxygenated, $p(O_2) = 0.95$ atm	.75
O_2/OH^-	1.23	Aerated, $p(O_2) = 0.2$ atm	.73

As is evident from the ionic composition Table 2.1, seawater is a complex solution. Each of these dissolved species contributes to the ozone demand, especially readily oxidizable species, such as the halides. Organics, amines and/or impurities (sulfides, iron(II), or manganese(II) ions) are present and increase the ozone demand of the seawater system.

The Bromide reaction in ozonated seawater is very important. Table 2.3 lists various bromine species and their chemical symbols. Figure 2.2 provides a pictorial representation of bromine reactions in ozonated seawater.[2]

Table 2.3 Bromine Species

Symbols	Species
Br	Bromine
Br^-	Bromide
BrO^-	Hypobromite
BrO_2^-	Bromite
BrO_3^-	Bromate
HOBr	Hypobromous Acid

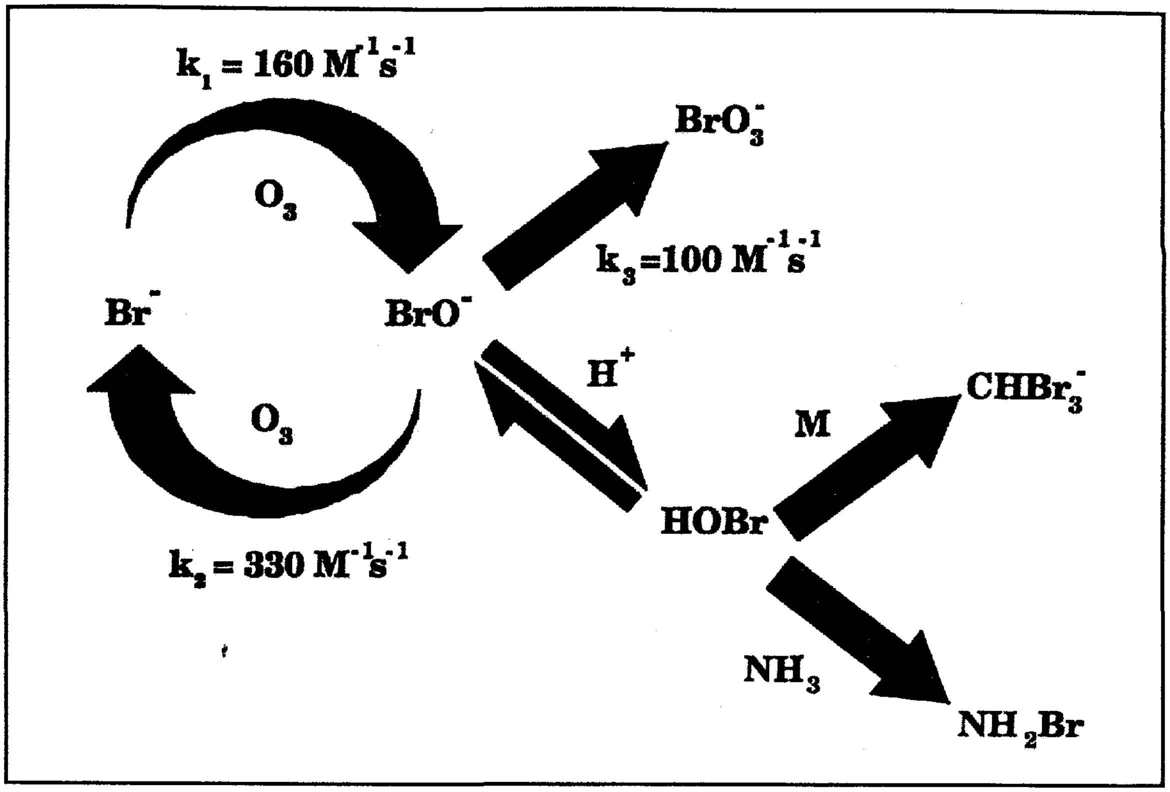


Figure 2.2 Bromine Reactions in Ozonated Seawater

In a manner similar to the oxidation reaction of bromide by hypochlorite to form hypobromite in chlorinated water, equation 8, ozone oxidizes bromide to form the hypobromite in ozonated seawater.

$$O_3 + Br^- \longrightarrow O_2 + BrO^- \qquad k_1 = 160\ M^{-1}s^{-1} \qquad (1)$$

Once the BrO^- is formed, it can proceed along one of three reaction routes. The first is an ozone depleting loop by recombining with molecular ozone to again form bromide.

$$O_3 + BrO^- \longrightarrow 2O_2 + Br^- \qquad k_2 = 330\ M^{-1}s^{-1} \qquad (2)$$

In the second possible reaction the hypobromite ion associates with an H+ ion and forms hypobromous acid, HOBr, an effective disinfectant.

$$H^+ + BrO- \longrightarrow HOBr \qquad (3)$$

The third hypobromite reaction involves the oxidation of hypobromite to form bromate.

$$2O_3 + BrO^- \longrightarrow 2O_2 + BrO_3^- \qquad k_4 = 100\ M^{-1}s^{-1} \qquad (4)$$

With the formation of the bromate, the ozone bromide reactions cease. Bromate is not a desirable by-product. It is not an effective disinfectant and its effect on the health of wild life is in question.

Ozone can also react with the chloride in the seawater. Ozone oxidizes chloride ions to form hypochlorite in a manner similar to the bromide and associated reactions.

$$O_3 + Cl^- \longrightarrow O_2 + ClO^- \qquad k_5 = 0.003\ M^{-1}s^{-1} \qquad (5)$$

$$O_3 + ClO^- \longrightarrow 2O_2 + Cl^- \qquad k_6 = 110\ M^{-1}s^{-1} \qquad (6)$$

$$2O_3 + ClO^- \longrightarrow 2O_2 + ClO_3^- \qquad k_7 = 30\ M^{-1}s^{-1} \qquad (7)$$

The rate constant (k_1) for the oxidation of bromide is much higher than for the oxidation of the chloride ions (k_5), therefore the hypobromite (1) will form more readily than the hypochlorite (5). The hypochlorite that is produced very rapidly oxidizes the bromide ions to form hypobromite (8).

$$ClO^- + Br^- \longrightarrow Cl^- + BrO^- \qquad k_8 = 6.7E3\ M^{-1}s^{-1} \qquad (8)$$

The hypobromite can react by equation 4 to form bromate. Solutions containing both bromide (Br^-) and chloride (Cl^-) ions reflect higher levels of bromate than solutions containing only the bromide ion. Hypochlorite in ozonated seawater solutions tends to be low. As a point of interest, hypochlorous acid (HClO) kills bacteria in chlorinated water and compounds generated during the reactions with the bacteria, such as CH_3NHCl, are what gives the water its characteristic "chlorine" odor.[21]

2.3 Crevice Corrosion

Most crevice corrosion failures occur in stainless steel alloys in neutral-to-acid solutions with chloride or ions containing chlorine.[3] This is an important consideration in the design of marine equipment and structures.[3] The most general type of crevice corrosion involves the rapid penetration and the retention of corrosive solutions within the crevice.

The usual appearance of crevice corrosion is broad, shallow depressions. Since most of the corrosion occurs at the beginning of the crevice, there is the potential for pitting corrosion near the mouth of very tight crevices. The level of corrosion diminishes the further into the interior of the crevice and the surface outside the crevice is passive and corrosion resistant.[3]

Research indicates that the tighter the crevice the greater the crevice corrosion. Metal-polymer crevices are tighter than metal-metal crevices so, all factors being equal, one would expect greater crevice corrosion for metal-polymer environments. Galvanic corrosion between two dissimilar metals is a different corrosion mechanism which can occur in metal-metal crevices. It must be treated as a separate issue when analyzing crevice corrosion.

Crevice corrosion is a form of rapid corrosion involving a nonuniform, local attack. The basic mechanism of corrosion in the crevice is caused by differential aeration and chloride concentration cells, which initiate and then propagate crevice corrosion. The initiation or breakdown potential is very dependent on crevice geometry and tightness. There are no reproducible recorded potential values.

The general overall corrosion reaction, occurring in and outside of the crevice, involves the dissolution of metal (M) and the reduction of oxygen to hydroxide ions.[4]

Oxidation $M \longrightarrow M^+ + e$

Reduction $O_2 + 2H_2O + 4e \longrightarrow 4OH^-$

Crevice corrosion initiates by the consumption of the limited supply of dissolved oxygen in the crevice.[3,4] The depletion of oxygen inside the crevice impairs passivity and increases the metal cation (M^+) concentration inside the crevice, which in turn attracts chloride ions Cl^- from the bulk solution.[3,4] With a relatively endless supply of chloride ions and acid hydrolysis, there is an increase in acid chloride levels inside the crevice by the following reaction: [3,4]

$$M^+Cl^- + H_2O \longrightarrow MOH\downarrow + HCl$$

where MOH is a weak base and the acid chloride is a strong acid. The metal inside the crevice acts as a small localized anode to the larger surface cathode in the bulk solution.[3,4] By the continued migration of Cl^- and hydrolysis in the crevice, the dissolution rate of the metal increases in an accelerating, autocatalytic process.[3,4] Empirical studies have observed chloride levels from 3 to 10 times greater in the crevice, relative to the bulk solution in neutral dilute sodium chloride solutions.[4]

Crevice corrosion can be prevented or at least minimized in a number of ways: (1) parts can be engineered and/or manufactured to eliminate the crevices; (2) joining of parts can be done by welding rather than by fixturing; (3) crevices can be filled in with weld or other material to eliminate the crevice; (4) maintaining a less aggressive environment in areas where crevices cannot be prevented; (5) lowering the chloride concentration, decreasing the acidity, and decreasing the temperature to provide a more hospitable environment; (6) material selection, i.e., selecting alloys and materials that are more crevice corrosion resistant, including impervious gaskets rather than porous ones; and (8) inspecting equipment and remove deposits.[3,4]

2.4 Fluorine

Fluorine is the most reactive of all the elements, due primarily to its weak F-F bond. Bond energy of fluorine is only 153 kJ/mol, compared to a chlorine bond energy of 243 kJ/mol.[21] Fluorine reacts with all other elements except for He, Ar, and Ne. Its reduction potential ($E°_{red}$) equals +2.889V and when it reacts with nickel it forms a tough fluoride film, NiF_2, which protects the surface from further corrosion.[21] Fluorine is stored in containers made of alloys containing Ni. Chlorine is almost as reactive, $E°_{red}$ equals +1.358. Chlorine reacts with almost all metals, although often requiring heat for the reactions to proceed.[21]

The most abundantly produced hydrogen halides in the United States are hydrogen fluoride (HF) and hydrogen chloride (HCl). More commonly known in their aqueous states as hydrofluoric and hydrochloric acids, respectively. Hydrofluoric is a weak acid, incompletely disassociating in water while hydrochloric is a strong acid.[21]

2.5 Titanium

Titanium, the ninth most abundant element in the earth's crust, is highly reactive, which appears contrary to its relatively inert corrosion behavior. The reason for this is a continuous, stable, protective and adherent passive oxide layer.[3,5] Once the oxide develops it generally does not corrode further. In another words, titanium oxidizes readily but is very corrosion resistant. This is due primarily to the resiliency of the oxide and this makes titanium a very cathodic or noble metal.[4,5] In the galvanic series of commercial metals and alloys in seawater, titanium is listed fourth after platinum, gold, and graphite.[4] Titanium oxides (TiO, Ti_2O_3 and TiO_2) are produced at all pH ranges. The oxide is typically transparent but if the titanium is heated with restricted access to air, a brilliant blue surface can be formed.[5] This blue film infers the presence of titanium oxide.[5]

Titanium oxide has high chemical resistance, especially at low temperatures. There are several chemicals, however, that degrade its relatively inert surface. Strong reducing acids such as hydrochloric and sulfuric can affect the passivity of the surface to corrosion, depending on the purity, temperature, and concentration of the acid.[3,5] Fluoride ions complex titanium, and its alloys are severely attacked by hydrofluoric acid and fluoride solutions.[3,5] Red fuming nitric acid readily breaks down the passive film and generates pyrophoric corrosion products.[3]

In tests measuring the corrosion rates of metals and alloys, titanium showed no sign of pitting in quiet seawater (velocities less than 2 ft/s).[4,5] Even at increased velocities of water flow, titanium showed no signs of pitting.[4,5] Titanium also shows an inert behavior to crevice corrosion in quiet seawater.[4] Titanium, although of itself is not antifouling, shows no signs of promoted pitting or crevice corrosion in the presence of fouling organisms.[5]

Titanium alloys develop crevice corrosion in oxidizing chloride or other halide solutions at temperatures above 70°C, in tight crevices of correct geometry.[3,4] Titanium is the only metal that appears to have consistent corrosion resistance to hypochlorite.[3] It is also resistant to other oxidizing acids and salts such as perchloric and hypochlorous acids, and chlorine and chloride solutions, where titanium is highly resistant to pitting.[3] Unalloyed titanium, commercial ASTM grade-2, is used in line processing equipment and storage tanks.[3] It is the single most used alloy in corrosion resistant applications.[10]

As mentioned, titanium dioxide is readily formed on any exposed surface of titanium. Some metals and metallic compounds (i.e., magnesium oxide) are good ultraviolet (UV) radiation reflectors and are added to the polymer matrix to provide UV protection.[6] Titanium dioxide, on the other hand, demonstrates low UV reflectance, and tends to photosensitize a host polymer.[6]

2.6 Polymers

Polymers, commonly known as plastics, are present in our everyday life as well as utilized in highly specialized applications.

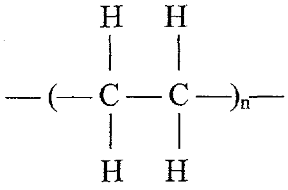
Some of the standard tests for a plastic's physical properties are: (1) tensile (ASTM D-638), including yield stress, ultimate and tensile strengths and percent ultimate elongation at break; (2) flexural (ASTM D-790), giving the flexural modulus and strength; (3) heat deflection temperature of a plastic under a load (ASTM D-648); (4) impact resistance or Izod impact test (ASTM D-256); (5) creep or deformation under a load over a period of time; (6) fatigue, under cyclic loading; arc resistance (ASTM D-495); and (7) dielectric strength (ASTM D-149).[8]

Polymeric materials are said to be viscoelastic, meaning possessing the properties of elastic solids and viscous fluids.[11] This behavior provides many polymers with rather low creep resistance. Creep occurs from the stretching, slipping, and uncoiling of the polymer chains under load.[11] Creep traditionally occurs under relatively low stress, but over an extended period of time.[11] Increased stress, temperature, and load time can all increase the amount of creep strain (deformation) in polymers.[11]

Many polymeric materials are sensitive to ultraviolet radiation. The reason for the degradation is found in the closeness of the energy intensity of the UV light to the bonding energy between most of the polymer atoms.[11] The exposure of the polymer to the UV light will break bonds between these atoms, weakening the molecules and the chains.[11]

2.6.1 Polyethylene High Density (PEHD)

Polyethylene is a very significant polymer which was first polymerized in England in 1939[17]. It is the largest volume polymer used in the United States,[9] and the largest volume thermoplastic in the world.[6] Its appeal stems from the ability to exist in linear form, as well as with side chains. It has applications as low and higher density structures. It is predominately a thermoplastic and is a member of the alkane group having the structural formula:



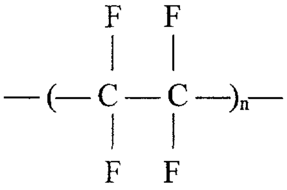
$$-\left(-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\overset{\displaystyle H}{\underset{\displaystyle H}{C}}-\right)_n-$$

There are four types of polyethylene, differentiated by molecular weight, density, and number of side chains. They are ultrahigh-density polyethylene (UHDPE), high-density polyethylene (HDPE or PEHD), linear low-density polyethylene (LLDPE), and low-density polyethylene (LDPE).[9] Many blends and copolymers are made from these four types of PE and are often copolymerized with other polymers.[9]

The higher grade, or molecular weight, polyethylenes have improved mechanical and strength properties such as toughness, tensile strength, and a higher softening temperature.[9] The lower grade polyethylenes tend to be more resistant to stress corrosion cracking and exhibit higher ductility.[9] Specific property values can vary significantly depending on the type of PE.[6,17]. Its desirable qualities are low cost, toughness, almost zero water absorption, excellent chemical and electrical resistance, and low coefficient of friction.[9] Typical uses are as piping, containers, film and bag materials, cable insulation, and automobile parts.[6,9] To provide protection against ultraviolet degradation carbon black is added to Polyethylene.

2.6.2 Teflon™

The International Union of Pure and Applied Chemistry (IUPAC) name for Teflon™ or poly(tetrafluoroethylene) (PTFE) is poly-(difluoromethylene) with a structure similar to polyethylene, but with the hydrogen replaced by fluorine:



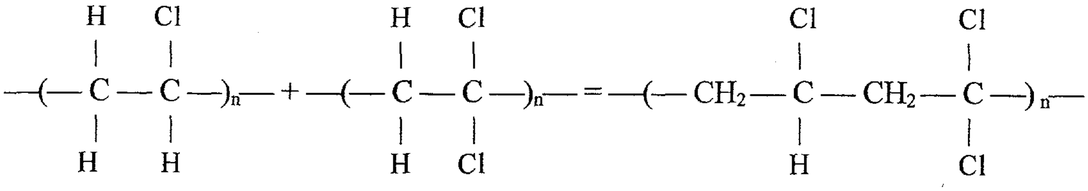
$$-(-\overset{F}{\underset{F}{C}}-\overset{F}{\underset{F}{C}}-)_n-$$

Teflon™ is processed by the emulsion free-radical polymerization of tetrafluoroethylene.[17] It is very dense (2.1 to 2.3 g/cm^3) with a high molecular weight and is difficult to process due to its extremely high crystalline structure and high crystalline-melting temperature (327°C).[9,11,17] It is one of the most important fluoropolymers because of its properties: high temperature stability, low temperature flexibility, extremely low coefficient of friction, low dielectric constant and dissipation factor, and chemical inertness.[9, 11,17] PTFE has a low tensile strength, between 2000-6500 psi, and a low ductility of about 3%.[9,10] PTFE tends to creep under stress especially at elevated temperatures.[10] Teflon's™ tendency to creep may be an important aspect to this current study. Elemental sodium removes fluorine from the PTFE polymer molecule.[10]

Some of its applications are as a sintered coating or additive to increase the lubricity of a material.[9,11] Fluorine makes the polymer inherently non-flammable for use as electrical insulators, in bearing assemblies, and in aerospace industry devices.[11] Its tightly held electrons enhance its properties as an electrical insulator.[11] It is also used as gasket and piping material, and is even utilized in the biomedical field for body part replacements.[9]

2.6.3 Saran

Saran is a copolymer composed of vinyl chloride and vinylidene chloride.[19]



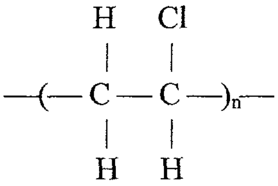
$$-\left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\right)_n- + -\left(-\underset{H}{\overset{H}{C}}-\underset{Cl}{\overset{Cl}{C}}-\right)_n- = -\left(-CH_2-\underset{H}{\overset{Cl}{C}}-CH_2-\underset{Cl}{\overset{Cl}{C}}-\right)_n-$$

vinyl chloride **vinylidene chloride** **Saran**

It is used predominately as a film wrap.

2.6.4 Polyvinyl chloride (PVC)

PVC is polymerized by the addition (free radical) method. [11]



$$-\left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{Cl}{C}}-\right)_n-$$

When PVC is unplasticized it is hard, brittle, and called "rigid PVC". It is used as piping and for other applications requiring its strength and rigidness.[11] Plasticized PVC is soft and pliable. It is most often referred to as "vinyl"[11] and has applications in car interiors, three-ring binders, structural siding, and flexible bottles. [11] PVC generates HCl gas when burned, which is toxic, but which also extinguishes the flames. Making both vinyl and rigid PVC flame retardant. [11]

PVC is a UV sensitive polymer and is affected by photo- and thermo-oxidation degradation. Both of these problems can be handled, at least in part, through the addition of UV and oxidation stabilizers.[11] The process of dehydrochlorination appears to be the underlying degradation process in which oxygen and oxygenated products act as initiators.[6]

A deleterious by-product of photochemical degradation at ambient temperatures is HCl, which in turn accelerates the PVC breakdown.[6] Dehydrochlorination is currently considered by many to proceed by a radical process but the catalytic effect of HCl is not fully understood.[6] Oxygen can have a bleaching effect caused by radical oxidation of long chain polymers. [6]

PART 3
EXPERIMENTAL PROCEDURE

3.1 Sample Preparation

3.1.1 Weight Loss Samples

Eighteen samples of three polymeric materials polyethylene (PE), Polyvinyl chloride (PVC), and Teflon™ (PTFE) were prepared by cutting 6.45 cm^2 (1 in.^{2}) samples on a band saw and then deburring with a sharp edge. A small hole was drilled in the corner of each weight loss sample to allow for fixturing. The fifty-four samples were ultrasonically cleaned, rinsed with distilled water, dried, and weighed before fixturing and insertion into the seawater baths. Weights before immersion are given in Table 3.1.

Table 3.1 Original Weights

Sample #	PVC (gms)	PEHD (gms)	PTFE (gms)
1	5.54238	3.51152	4.51962
2	5.60006	3.52775	4.30584
3	5.47454	3.39600	4.33435
4	5.49121	3.65195	4.39567
5	5.53827	3.64025	4.51303
6	5.58490	3.62018	4.39204
7	5.60062	3.53310	4.33615
8	5.60822	3.61648	4.39184
9	5.65299	3.45594	4.27034
10	5.55974	3.50750	4.51043
11	5.51540	3.55332	4.57365
12	5.67110	3.52800	4.39657
13	5.45825	3.61190	4.44373
14	5.58372	3.57511	4.48468
15	5.53014	3.55165	4.46535
16	5.58509	3.53889	4.34647
17	5.54332	3.57200	4.20743
18	5.60960	3.58137	4.40939

After the initial weighing, the samples were fixtured by passing a Teflon™ string through the small hole in the corner of each sample. The other end of the string was tied to a small Teflon™ ring. A glass rod was then passed through each Teflon™ ring and the samples were submerged in their respective tanks. Each glass rod held 4 - 8 fixtured weight loss samples.

3.1.2 Crevice Samples

Forty-eight titanium grade-2 corrosion coupons were cut from a 0.159 cm (0.06 in.) thick plate to 2.5 x 5.1 cm (1.0 x 2.0 in.). The composition of the Ti grade-2 is given in Table 3.2. A 0.95 cm (0.38 in.) hole was drilled in the center of the samples and then the samples were deburred, lapped, and the "front " of each sample was engraved with a sample number.

Table 3.2 Titanium Grade-2 Composition

	C	Fe	N	O	H	Ti
Ti grade-2	0.02	0.1	0.012	0.12	0.001	bal.

The samples were ultrasonically cleaned using distilled water and then rinsed with distilled water. The polymer or titanium washers were fixtured to the crevice sample as shown in Figure 3.1. All the polymer washers had flat surfaces except for the Teflon™ washers which were crenelated on one side, see Figure 3.1. All the fixturing components including the titanium washers, titanium bolt, titanium nuts, and crenelated washers were ultrasonically cleaned, rinsed, and dried before assembling.

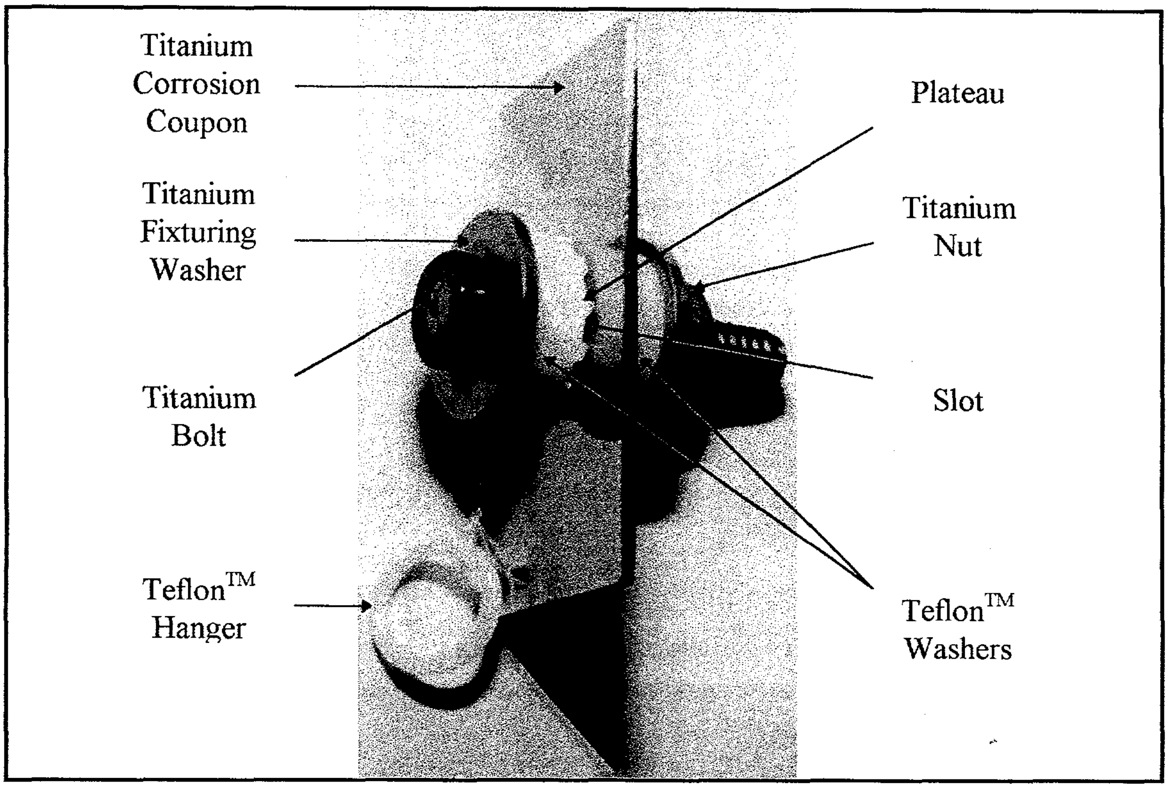


Figure 3.1 Crevice Sample Fixture

The sample fixtures were prepared as follows. Using latex gloves the bolt was wrapped with Teflon™ tape to prevent electrical continuity between the bolt and the corrosion coupon. Thereby isolating the coupon from the rest of the fixture except for contact points with the washers. The experiment was divided into five different tests, listed in Tables 3.3a and 3.3b.

Table 3.3a Crevice Corrosion Tests 1 - 4

Sample #	Tank	Washer Type	Proposed Time	Comments
1-1	Ozonated	Titanium	4 weeks	Bolts wrapped with Teflon™ Tape
1-2	Ozonated	Titanium	16 weeks	Bolts wrapped with Teflon™ Tape
1-3	Ozonated	Titanium	20 weeks	Bolts wrapped with Teflon™ Tape
1-4	Ozonated	Titanium	26 weeks	Bolts wrapped with Teflon™ Tape
1-5	Ozonated	Titanium	26 weeks	Bolts wrapped with Teflon™ Tape
1-6	Ozonated	Titanium	26 weeks	Bolts wrapped with Teflon™ Tape
1-7	Aerated	Titanium	4 weeks	Bolts wrapped with Teflon™ Tape
1-8	Aerated	Titanium	16 weeks	Bolts wrapped with Teflon™ Tape
1-9	Aerated	Titanium	20 weeks	Bolts wrapped with Teflon™ Tape
1-10	Aerated	Titanium	26 weeks	Bolts wrapped with Teflon™ Tape
2-1	Ozonated	PVC	26 weeks	Bolts wrapped with PE
2-2	Ozonated	PVC	26 weeks	Bolts wrapped with PE
2-3	Ozonated	PVC	26 weeks	Bolts wrapped with PE
2-4	Aerated	PVC	26 weeks	Bolts wrapped with PE
2-5	Aerated	PVC	26 weeks	Bolts wrapped with PE
2-6	Aerated	PVC	26 weeks	Bolts wrapped with PE
3-1	Ozonated	PE	26 weeks	Bolts wrapped with PE
3-2	Ozonated	PE	26 weeks	Bolts wrapped with PE
3-3	Ozonated	PE	26 weeks	Bolts wrapped with PE
3-4	Aerated	PE	26 weeks	Bolts wrapped with PE
3-5	Aerated	PE	26 weeks	Bolts wrapped with PE
3-6	Aerated	PE	26 weeks	Bolts wrapped with PE
4-1	Ozonated	Saran wrap	26 weeks	Bolts wrapped with Saran
4-2	Ozonated	Saran wrap	26 weeks	Bolts wrapped with Saran
4-3	Ozonated	Saran wrap	26 weeks	Bolts wrapped with Saran
4-4	Aerated	Saran wrap	26 weeks	Bolts wrapped with Saran
4-5	Aerated	Saran wrap	26 weeks	Bolts wrapped with Saran
4-6	Aerated	Saran wrap	26 weeks	Bolts wrapped with Saran

Table 3.3b Crevice Corrosion Test 5

Sample #	Tank	Washer Type	Proposed Time	Comments
5-1	Aerated	PTFE	4 weeks	Teflon™ washers reversed
5-2	Aerated	PTFE	16 weeks	Teflon™ washers reversed
5-3	Aerated	PTFE	20 weeks	Bolts wrapped with Teflon™ Tape
5-4	Aerated	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-5	Aerated	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-6	Ozonate	PTFE	26 weeks	Teflon™ washers reversed
5-7	Ozonate	PTFE	26 weeks	Teflon™ washers reversed
5-8	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-9	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-10	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-11	Aerated	PTFE	4 weeks	Bolts wrapped with Teflon™ Tape
5-12	Aerated	PTFE	16 weeks	Bolts wrapped with Teflon™ Tape
5-13	Aerated	PTFE	20 weeks	Bolts wrapped with Teflon™ Tape
5-14	Aerated	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-15	Aerated	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-16	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-17	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-18	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-19	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape
5-20	Ozonate	PTFE	26 weeks	Bolts wrapped with Teflon™ Tape

The fixtures were assembled submerged in a bath of artificial seawater to eliminate air bubbles in the crevices and to pre-wet the samples. The order of assembly onto the bolt was as follows: (1) the first titanium nut was screwed tight to the head of the bolt; (2) a Teflon™ string was attached between the head and the nut; (3) a Teflon™ ring was attached to the other end of the string; (4) a titanium washer was inserted; (5) the first crevice washer was positioned; (6) then the corrosion coupon; (7) followed by the second crevice washer; (8) the last titanium washer was inserted onto the bolt; (9) the last nut was screwed on and carefully turned an additional 3/4 turn past hand tight with a wrench; (10) each fixture was tested with a resistance meter to ensure lack of continuity between the coupon and the bolt; (11) the Teflon™ ring at the end of the string was inserted onto a glass rod along with 3 to 5 other sample fixtures; and (12) the glass rod, with the fixtures secured, was removed from the preparation bath and quickly hung in its perspective tank, Figures 3.1 and 3.2.

3.2 Solutions

3.2.1 Preparation

The artificial seawater solution was prepared by mixing 34.75 g of Forty Fathoms Bio-Crystals™ Marinemix per liter of distilled water. Two, 60 liter tanks were filled with 56 liters of the prepared solution. The Marinemix meets all the requirements and composition of artificial seawater as a replacement for natural seawater in accordance with ASTM D1141-90.[23] All tests were performed under room temperature conditions and typical room lighting from fluorescent fixtures and sunlight.

3.2.2 Aeration and Ozonation Delivery

General purpose laboratory supplied air was bubbled into the aerated tank for at least one week prior to sample insertion. The ozone for the ozonated tank was supplied by first generating oxygen using an AirSep® AS-12 oxygen generator operating at 55% of maximum output and at 69 kPa (10 psi) pressure. Approximately 90-95% oxygen, with the balance of nitrogen, was supplied to the ozone generator at a flow rate of 0.28 m/hr SCFH (standard cubic feet per minute). The ozone generator, an American Ozone™ GS2-14 ozone generator operated at 21 kPa (3 psi) pressure. At a power setting of 85%, it supplied 47 g O_3/m^3 (3.35 wt% O_3 in 90-95% O_2).

The air for the aerated seawater tank was delivered through norprene® tubing and a control valve. The ozone delivery, due to ozone's reactive nature, involved special fixturing. The tubing used was Teflon™ and norprene®, but only Teflon™ tubing was used inside the ozonated seawater tank. A special valved, glass-lined, stainless steel ball flow meter (range 0-2 SCFH) provided the ozone delivery of 0.03 m^3/hr (1 SCFH). At this flow rate the ozone delivery rate was 1.3 g O_3/hr with an oxygen delivery rate of 39 g O_2/hr.

After the two tanks were filled and the aeration and ozonation started, the tanks were sealed with unbleached polyvinyl chloride (PVC) covers secured with duct tape to the tops of the tanks. Provisions were made, via silicone sealed holes, for the insertion of the air or ozone supply line and the exhaust duct for the ozone tank. The excess ozone was exhausted out of the ozone tank using accordion type flexible vinyl ducting. Exhaust fans in the ducting expelled the ozone outdoors. The ozone exhaust was well below the Environmental Protection Agency (EPA) allowable exhaust limits. A 2 in. X 2 in. hole in one of the front corners of the cover allowed easy access for solution testing and solution maintenance. It was taped closed when not in use. See Figure 3.2 for ventilation and laboratory setup.

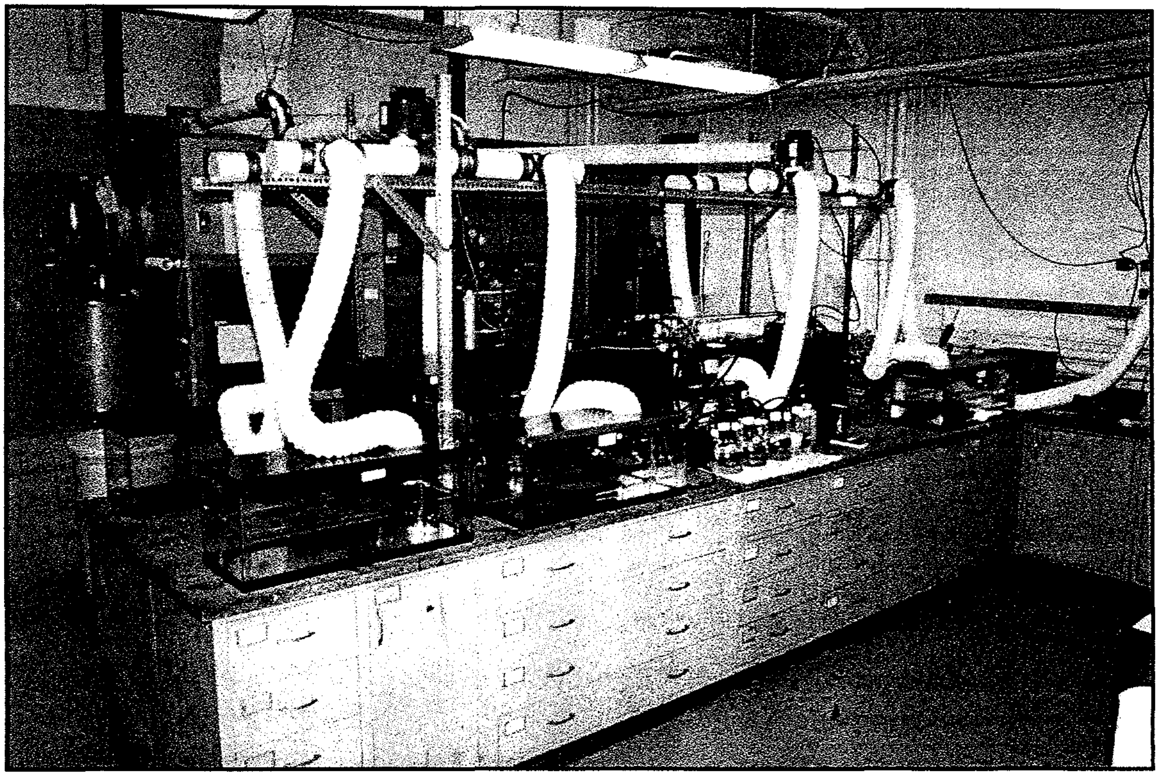


Figure 3.2 Tank and Ventilation Setup

3.2.3 Solution Testing and Maintenance

Before any of the test samples were placed into either of the solutions, the tanks were allowed to operate under aerating or ozonating conditions for a specific time to allow solution conditions to stabilize. In particular, the ozonated tank, required more maintenance to effectively meet the ozone demand of the various species in solution. Once the ozone demand was satisfied, the appropriate quantities of ozone could be made available for the corrosion samples.

The ozonated and aerated tank solutions were tested for pH and bromide concentrations. Bromide concentrations were maintained in the range of 800-860 mM/L (63-69 mg/L) throughout the experiment. The pH levels stabilized and remained at approximately 8.0. Ozone, hypohalites, and bromate concentrations were verified to be zero in the aerated tank. In the ozonated tank the bromate concentration was maintained between 82-89% of the total bromide. Hypobromous and hypobromite were from 0-5 % and free Br- between 10-15 % of the total bromide. Ozone levels were maintained between 0.3-0.4 mg/L.

Previous experience demonstrated that reaction by-products accumulate to undesirable levels in the ozonated tank. In order to maintain the chemical balance in the ozone tank, weekly removals of six liters of solution were performed and replaced with fresh artificial seawater solution, to maintain the chemical balance in the tank. Periodic titrations (Appendix B) were done on both tanks to ensure solution quality and suitable adjustments were made as warranted. Titrations were also performed when samples were removed.

3.3 Sample Removal and Analysis

All the weight loss samples were removed after 26 weeks of testing. They were rinsed with distilled water, allowed to air dry, reweighed, and compared to pretest weights. Results are given in Tables 4.1 through 4.3. The crevice samples were removed from their respective tanks based on the time schedule given in Tables 4.4a and b. Upon removal, the samples were rinsed with distilled water and allowed to air dry. Electrical resistivity was remeasured to ensure lack of continuity between the corrosion coupon and the metal fixture. Next, the fixtures were carefully disassembled. All of the components were rinsed a second time and allowed to air dry. Visual inspections were performed, comments were documented, low magnification photos were taken, and the samples were placed in a dessicator awaiting further chemical analysis and higher magnification photos. Scanning electron microscopic (SEM) photographs were taken of selected samples. Chemical analysis of the sample surfaces was performed using energy dispersive spectrometry (EDS), also known as energy dispersive x-ray (EDX) analysis. If visible corrosion was present, the pertinent parts of the fixture were then placed in the dessicator.

PART 4
RESULTS

4.1 Weight Loss Samples

All the samples lost weight to varying degrees except for the PVC samples in the aerated bath. The PVC in the aerated bath showed a net gain in weight of about 0.05%. Except for one of the PVC samples, which lost 2.18%, all the PVC samples in the ozonated tank lost approximately 0.4% of their original weights. The PEHD samples under aeration conditions showed an average weight loss of 0.03% and in the ozonated tank an average loss of 1.44%. Both PVC and PEHD tests showed a higher percentage weight loss than the Teflon™ samples in the ozonated seawater solution, approximately 0.5% for PVC, 1.4% for PEHD, and 0.03% for PTFE. The Teflon™ weight loss in the ozonated tank was similar to that in the aerated tank, between 0.025 - 0.03%.

The results of the polymer weight loss tests are presented in Tables 4.1, 4.2, and 4.3. Associated plots of the weight loss are given in Figures 4.1, 4.2, and 4.3. Based on the relatively small calculated standard deviations, the data show little variance. The only exception can be found in the ozonated PVC test. Due to PVC sample #1, the standard deviation of the PVC percent weight loss is 1.255863, which is considerably higher than the other tests. The PVC samples also experienced a whitening effect in the ozonated bath.

Although the results of the Teflon™ samples did not reflect a high percentage of weight loss, they did demonstrate that Teflon™ can degrade given the conditions of these tests. Teflon™ weight loss was consistent in both the aerated and ozonated tanks. The mechanisms responsible for the breakdown of the Teflon™ must be present in both of these solutions. Although Teflon™ will creep under an applied load and stress may enhance the degradation of Teflon™ these weight loss tests only indicate that PTFE will deteriorate in both types of seawater solutions. These tests do not provide evidence to substantiate whether stress is a contributing factor.

Table 4.1 Weight Loss Results for PVC

Sample #	Tank	Before	After	Net	% Weight
1	**Ozonated**	5.54238	5.4216	-0.12078	-2.17921
2	**Ozonated**	5.60006	5.5782	-0.02186	-0.39035
3	**Ozonated**	5.47454	5.4538	-0.02074	-0.37884
4	**Ozonated**	5.49121	5.4719	-0.01931	-0.35165
5	**Ozonated**	5.53827	5.5173	-0.02097	-0.37864
6	**Ozonated**	5.58490	5.5642	-0.0207	-0.37064
7	**Ozonated**	5.60062	5.5798	-0.02082	-0.37174
8	**Ozonated**	5.60862	5.5865	-0.02212	-0.39439
9	**Ozonated**	5.65299	5.6302	-0.02279	-0.40315
Average				-0.03223	-0.57985
Standard Deviation				0.069289	1.255863
10	**Aerated**	5.55974	5.5623	0.00256	0.046045
11	**Aerated**	5.51540	5.518	0.0026	0.047141
12	**Aerated**	5.67110	5.6735	0.0024	0.04232
13	**Aerated**	5.45825	5.4608	0.00255	0.046718
14	**Aerated**	5.58372	5.5865	0.00278	0.049788
15	**Aerated**	5.53014	5.5342	0.00406	0.073416
16	**Aerated**	5.58509	5.587	0.00191	0.034198
17	**Aerated**	5.54332	5.5459	0.00258	0.046543
18	**Aerated**	5.60960	5.6123	0.0027	0.048132
Average				0.002682	0.048256
Standard Deviation				9.9E-05	0.001475

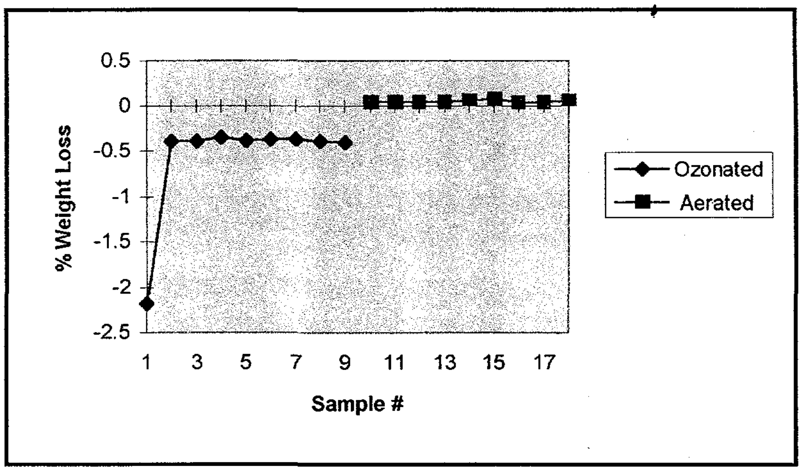


Figure 4.1 Percent Weight Loss for PVC

Table 4.2 Weight Loss Results for PEHD

Sample #	Tank	Before	After	Net	% Weight
1	**Ozonated**	3.51152	3.4624	-0.04912	-1.39882
2	**Ozonated**	3.52775	3.477	-0.05075	-1.43859
3	**Ozonated**	3.39600	3.3483	-0.0477	-1.40459
4	**Ozonated**	3.65195	3.6001	-0.05185	-1.41979
5	**Ozonated**	3.64025	3.5874	-0.05285	-1.45182
6	**Ozonated**	3.62018	3.5697	-0.05048	-1.39441
7	**Ozonated**	3.53310	3.4804	-0.0527	-1.49161
8	**Ozonated**	3.61648	3.5646	-0.05188	-1.43454
9	**Ozonated**	3.45594	3.4042	-0.05174	-1.49713
Average				-0.05101	-1.43681
Standard Deviation				0.001853	0.069514
10	**Aerated**	3.50750	3.5064	-0.0011	-0.03136
11	**Aerated**	3.55332	3.5527	-0.00062	-0.01745
12	**Aerated**	3.52800	3.5223	-0.0057	-0.16156
13	**Aerated**	3.61190	3.6114	-0.0005	-0.01384
14	**Aerated**	3.57511	3.5748	-0.00031	-0.00867
15	**Aerated**	3.55165	3.5511	-0.00055	-0.01549
16	**Aerated**	3.53889	3.5384	-0.00049	-0.01385
17	**Aerated**	3.57200	3.5719	-0.0001	-0.0028
18	**Aerated**	3.58137	3.5807	-0.00067	-0.01871
Average				-0.00112	-0.03153
Standard Deviation				0.000304	0.008947

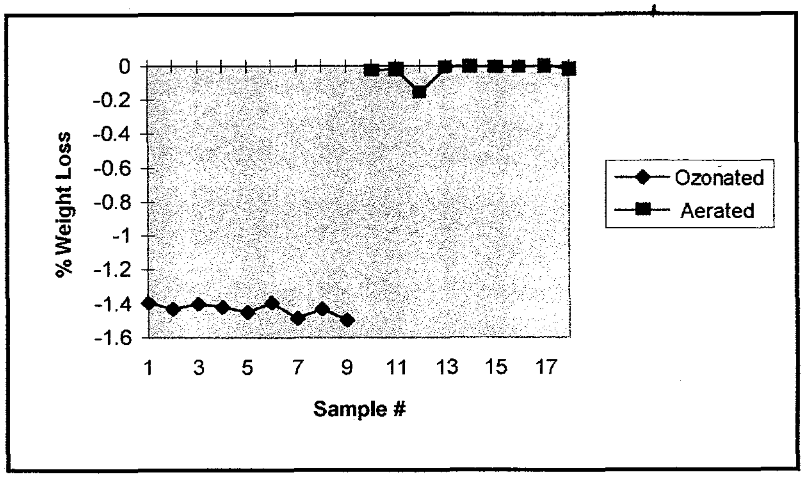


Figure 4.2 Percent Weight Loss for PEHD

Table 4.3 Weight Loss Results for PTFE

Sample #	Tank	Before	After	Net	% Weight
1	Ozonated	4.51962	4.5181	-0.00152	-0.03363
2	Ozonated	4.30584	4.3048	-0.00104	-0.02415
3	Ozonated	4.33435	4.3331	-0.00125	-0.02884
4	Ozonated	4.39567	4.3946	-0.00107	-0.02434
5	Ozonated	4.51303	4.5118	-0.00123	-0.02725
6	Ozonated	4.39204	4.3909	-0.00114	-0.02596
7	Ozonated	4.33615	4.3347	-0.00145	-0.03344
8	Ozonated	4.39184	4.3905	-0.00134	-0.03051
9	Ozonated	4.27034	4.2689	-0.00144	-0.03372
Average				-0.00128	-0.02909
Standard Deviation				5.66E-05	6.35E-05
10	Aerated	4.51043	4.5093	-0.00113	-0.02505
11	Aerated	4.57365	4.5727	-0.00095	-0.02077
12	Aerated	4.39657	4.3955	-0.00107	-0.02434
13	Aerated	4.44373	4.4422	-0.00153	-0.03443
14	Aerated	4.48468	4.4838	-0.00088	-0.01962
15	Aerated	4.46535	4.4641	-0.00125	-0.02799
16	Aerated	4.34647	4.3452	-0.00127	-0.02922
17	Aerated	4.20743	4.2063	-0.00113	-0.02686
18	Aerated	4.40939	4.4082	-0.00119	-0.02699
Average				-0.00116	-0.02614
Standard Deviation				4.24E-05	0.001368

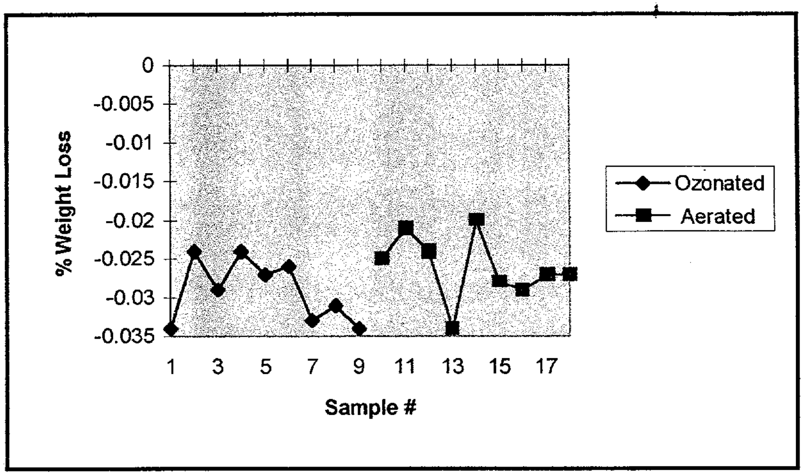


Figure 4.3 Percent Weight Loss for PTFE

The overall results from the weight loss tests indicate that the polymeric materials experienced weight loss to varying degrees when exposed to ozonated seawater solution over an extended period of time. The weight loss in the Teflon™ test, refer to Figure and Table 4.3, shows no difference between the ozonated and aerated tanks.

4.2 Crevice Samples

During experimentation, the immersion time of most of the samples was extended to obtain a better representation of the corrosion effects. Tables 4.4a and 4.4b list the removal times for the crevice samples and brief comments noting surface conditions upon fixture disassembly. All of the crevice samples immersed in the aerated seawater solution tank lacked visible indications of corrosion. While most of the ozonated samples had visible signs of corrosion product. The results of EDS analysis of all the surfaces examined, both aerated and ozonated, showed to varying degrees the presence of silicon and carbon. These elements are residual from the pretest surface lapping using a silicon carbide blade.

4.2.1 Titanium Washers

The data of the titanium washer crevice tests verified previous test results. There were no indications of crevice corrosion on the titanium coupons. Figure 4.4 is an SEM photograph of the ozonated titanium surface crevice area of the ozonated sample #1-1 (front). Figure 4.5 is an SEM photograph of the crevice area on the titanium surface of the aerated sample #1-7 (front). Iron was not found on either the ozonated or aerated surfaces as was recorded in previous Rensselaer tests.[2]

The crevice geometry using titanium washers is apparently not conducive to the production of crevice corrosion. Since there was corrosion on coupons using fluorinated (PTFE), chlorinated (PVC), and hydrocarbon (PEHD) polymeric washers, the crevice geometry produced by the polymers must play a critical role in the generation of crevice corrosion. The fact that these polymers are high creep materials may be influential in generating the necessary crevice geometry.

Table 4.4a Crevice Sample Removal Times and Observations. Tests 1-4

Sample #	Tank	Washer Type	Actual Time	Observations
1-1	Ozonated	Titanium	26 weeks	No Indication of Corrosion
1-2	Ozonated	Titanium	26 weeks	No Indication of Corrosion
1-3	Ozonated	Titanium	26 weeks	No Indication of Corrosion
1-4	Ozonated	Titanium	26 weeks	No Indication of Corrosion
1-5	Ozonated	Titanium	26 weeks	No Indication of Corrosion
1-6	Ozonated	Titanium	4 weeks	No Indication of Corrosion
1-7	Aerated	Titanium	26 weeks	No Indication of Corrosion
1-8	Aerated	Titanium	26 weeks	No Indication of Corrosion
1-9	Aerated	Titanium	26 weeks	No Indication of Corrosion
1-10	Aerated	Titanium	4 weeks	No Indication of Corrosion
2-1	Ozonated	PVC	26 weeks	Light Brown Rings
2-2	Ozonated	PVC	26 weeks	Light Brown Rings
2-3	Ozonated	PVC	26 weeks	Light Brown Rings
2-4	Aerated	PVC	26 weeks	No Indication of Corrosion
2-5	Aerated	PVC	26 weeks	No Indication of Corrosion
2-6	Aerated	PVC	26 weeks	No Indication of Corrosion
3-1	Ozonated	PEHD	26 weeks	Blue Corrosion
3-2	Ozonated	PEHD	26 weeks	Blue Corrosion
3-3	Ozonated	PEHD	26 weeks	Green/Purple Corrosion
3-4	Aerated	PEHD	26 weeks	No Indication of Corrosion
3-5	Aerated	PEHD	26 weeks	No Indication of Corrosion
3-6	Aerated	PEHD	26 weeks	No Indication of Corrosion
4-1	Ozonated	Saran wrap	26 weeks	Blue/Brown Corrosion
4-2	Ozonated	Saran wrap	26 weeks	Spots of Blue Corrosion
4-3	Ozonated	Saran wrap	26 weeks	Spots of Blue Corrosion
4-4	Aerated	Saran wrap	26 weeks	No Indication of Corrosion
4-5	Aerated	Saran wrap	26 weeks	No Indication of Corrosion
4-6	Aerated	Saran wrap	26 weeks	No Indication of Corrosion

Table 4.4b Crevice Sample Removal Times and Observations. Test 5

Sample #	Tank	Washer Type	Actual Time	Observations
5-1	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-2	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-3	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-4	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-5	Aerated	PTFE	4 weeks	No Indication of Corrosion
5-6	Ozonated	PTFE	26 weeks	Blue Corrosion
5-7	Ozonated	PTFE	26 weeks	Blue Corrosion
5-8	Ozonated	PTFE	26 weeks	Blue Corrosion
5-9	Ozonated	PTFE	26 weeks	Corrosion
5-10	Ozonated	PTFE	26 weeks	Corrosion
5-11	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-12	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-13	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-14	Aerated	PTFE	26 weeks	No Indication of Corrosion
5-15	Aerated	PTFE	16 weeks	No Indication of Corrosion
5-16	Ozonated	PTFE	4 weeks	Impression of Washer
5-17	Ozonated	PTFE	16 weeks	Faint Indications
5-18	Ozonated	PTFE	26 weeks	Corrosion
5-19	Ozonated	PTFE	26 weeks	Blue/Brown Corrosion
5-20	Ozonated	PTFE	26 weeks	Corrosion

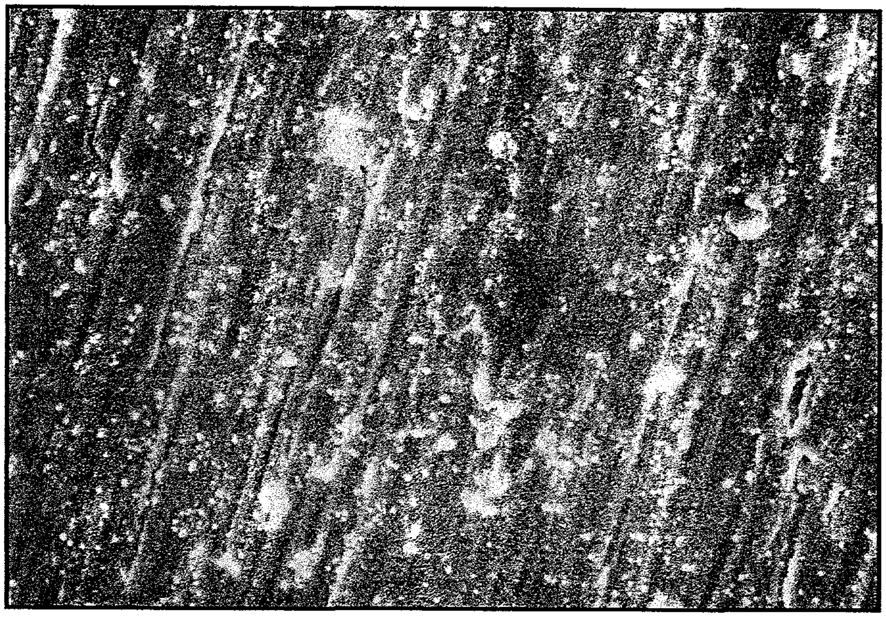


Figure 4.4 SEM Micrograph of Ozonated Ti Washer Sample #1-1 (Front). 1110X

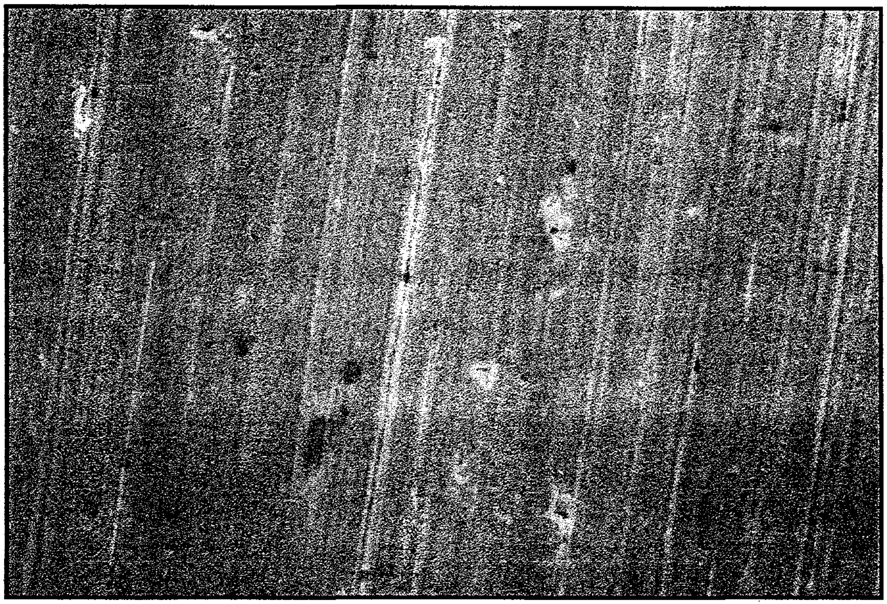


Figure 4.5 SEM Micrograph of Aerated Ti Washer Sample #1-7 (Front). 555X

4.2.2 PVC Washers

In the ozonated tank, the PVC washer crevice coupons had some visible corrosion. Photographs of sample #2-3 (front) are provided in Figures 4.6 and 4.7. The corrosion on the ozonated samples was limited. Faint, light brown rings rather than the blue/brown colors of the other polymer samples were evident. EDS analysis of the coupon surfaces found the presence of chlorine in these affected areas. The aerated samples, SEM photograph of sample #2-4 (front) given in Figure 4.8, showed no visible signs of corrosion. EDS analysis of the dark areas on the surface of sample #2-4 found no evidence of corrosion product.

The outer circumference of the PVC washers immersed in the ozonated bath turned white, while the PVC in the aerated solution did not. Probably a result of a bleaching effect due to dehydrochlorination in the presence of ozone. The weight loss PVC ozonated samples also whitened, but the outer surface of the washers were considerably whiter than the weight loss samples. Dehydrochlorination is probably a contributing factor to the corrosion process in these PVC washer test samples.

4.2.3 PEHD Washers

Figures 4.9 and 4.10, photographs of sample #3-3 (back), show strong corrosion rings on the ozonated PEHD sample, typical of this test group. The colors of the corrosion products were green/purple shades, similar to the corrosion colors of the PTFE crevice samples and much more pronounced than the brown coloring of the PVC crevice samples. EDS of the surface found spotty areas of relatively high levels of fluorine on one of the coupons and chlorine present on another. Figure 4.11 is an SEM photograph of the green/purple ring on the sample which showed fluorine. Location #1 on the photograph, the darkened area, contained fluorine, while location #2, the lighter area, showed no sign of fluorine. Figure 4.12 shows the surface of PEHD aerated sample #3-6 (front). The ring of corrosion product can be attributed to crevice corrosion involving the chloride ion.

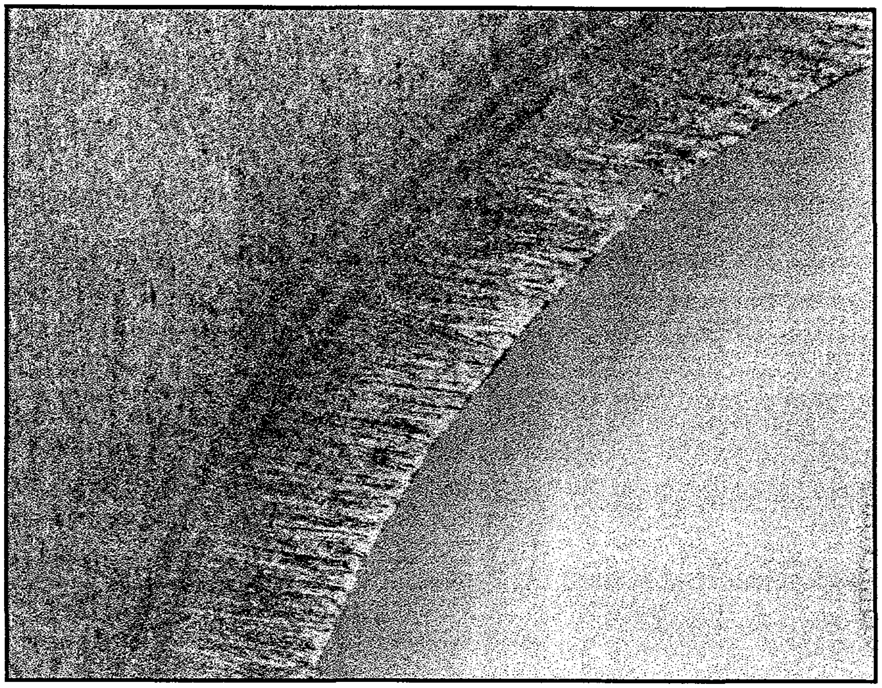


Figure 4.6 Ozonated PVC Sample #2-3 (Front)

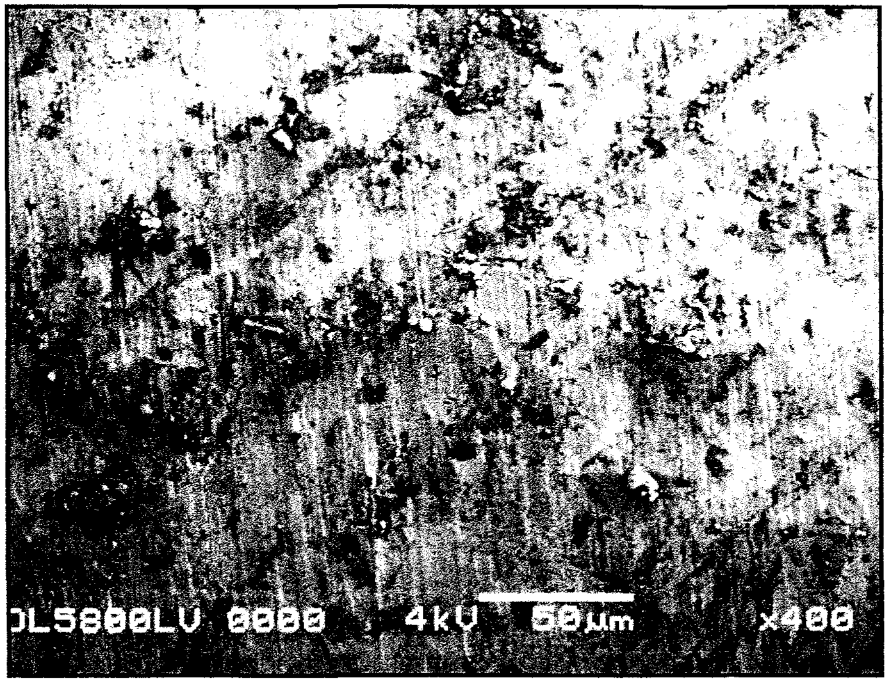


Figure 4.7 SEM Micrograph of Ozonated PVC Sample #2-3 (Front). 400X

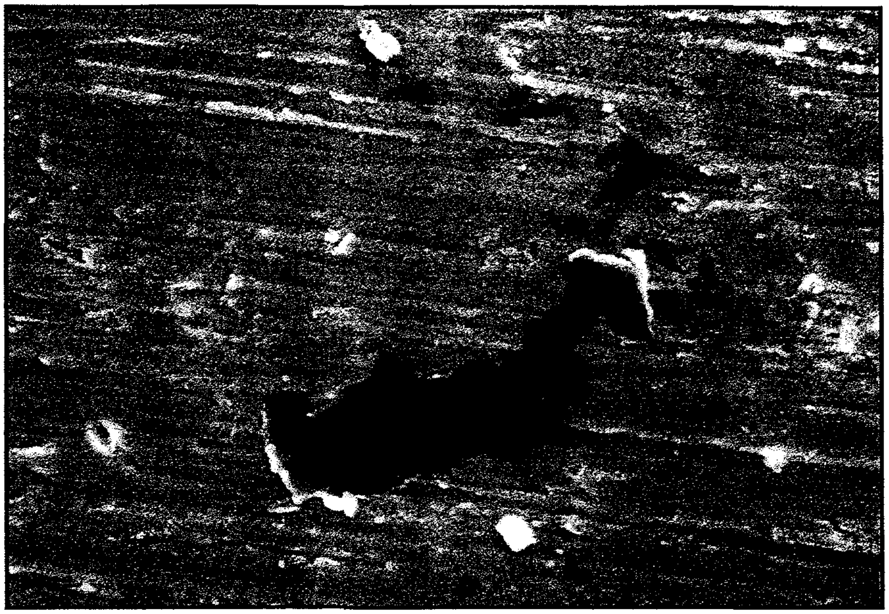


Figure 4.8 SEM Micrograph of Aerated PVC Sample #2-4 (Front). 1210X

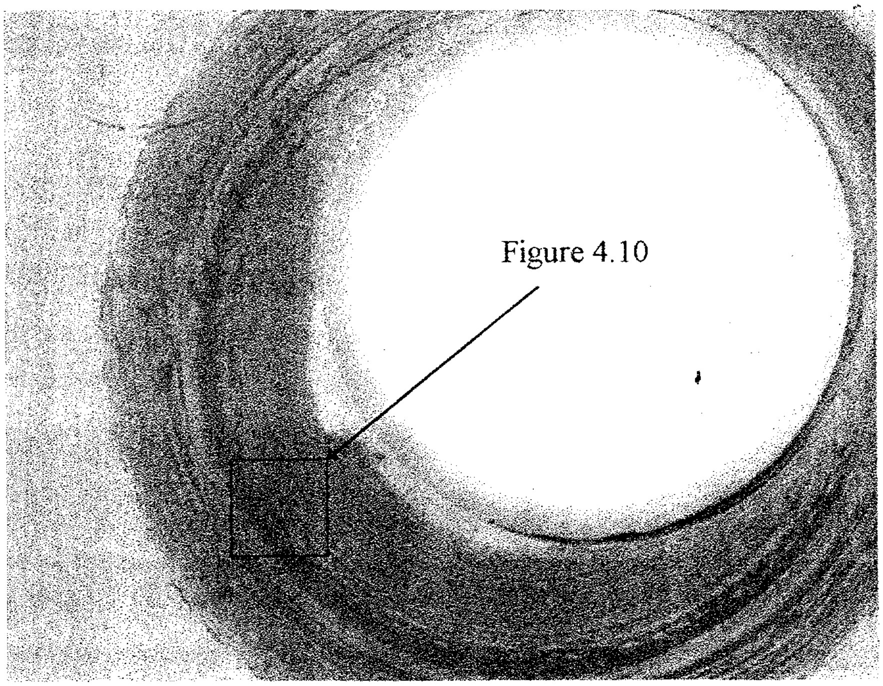


Figure 4.9 Ozonated PEHD Sample #3-3 (Back)

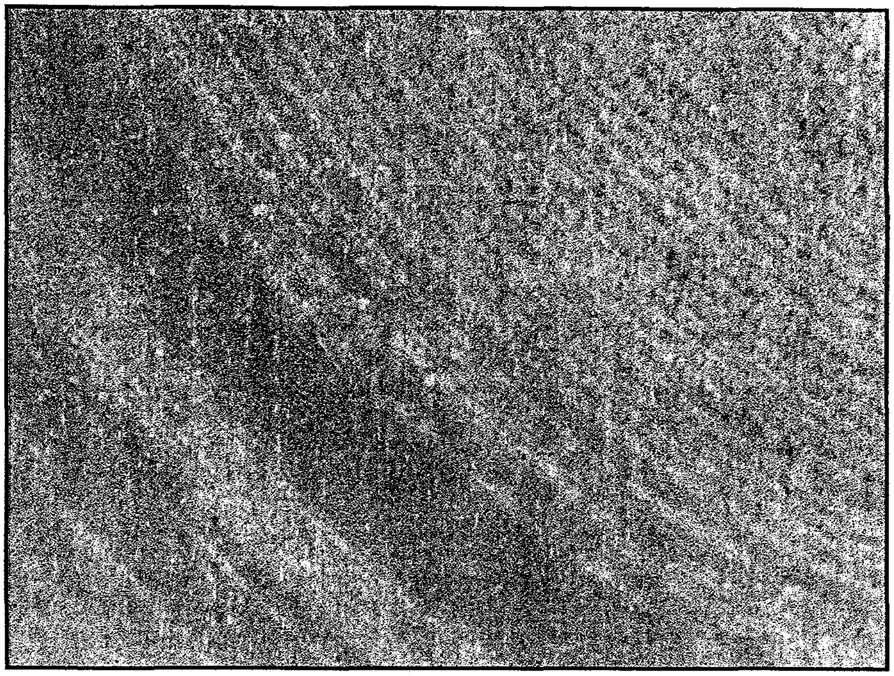


Figure 4.10 Ozonated PEHD Sample #3-3 (Back). Higher Magnification Photo of Highlighted Area in Figure 4.9.

Figure 4.11 SEM Micrograph of Ozonated PEHD Sample #3-3 (Back). 665X

Figure 4.12 SEM Micrograph of Aerated PEHD Sample #3-6 (Front). 1120X

The presence of fluorine in the corrosion product on the titanium surface of the ozonated PEHD sample #3-3 was unexpected. In addition to EDS analysis performed on all three samples, wavelength dispersive spectrometry (WDS) was used in an attempt to find fluorine on the two surfaces that did not demonstrate its presence under EDS analysis. Fluorine was not found on these two surfaces. Since fluorine is not present in PEHD, the fluoride ions must have been a contaminant on the surface during fixturing or after removal from the test bath, or fluorine entered the crevice from the bulk solution by a yet unknown mechanism. This mechanism maybe similar to the attraction of chloride ions into the crevice by the more familiar crevice corrosion mechanism. See Section 2.3 Crevice Corrosion.

4.2.4 Saran Washers

Figures 4.13 and 4.14 show the surface of a Saran generated crevice coupon, sample #4-1 (back), in the ozone seawater solution. Although the corrosion is much less uniform than the other corroded samples from the ozonated tank, the typical shades of blue are still distinct. EDS analysis of the surface did not indicate the presence of chlorine or fluorine in these affected areas. Despite the lack of detectable chlorine the mechanism for corrosion is most likely classical crevice corrosion involving chloride ions. Figure 4.15 is a micrograph of ozonated sample #4-1. The aerated samples had no indications of corrosion and EDS analysis found no corrosion products on the surface. Figure 4.16 is an SEM photograph of the aerated sample #4-5.

4.2.5 Teflon™ Washers

The ozonated Teflon™ crevice samples exhibited strong indications of crevice corrosion. Both Teflon™ samples whose crevices were generated by the crenelated side of the washers, as well as the crevices produced by inverting the Teflon™ washer and placing the flat surface of the washer on the titanium, showed high levels of corrosion. Sample #5-8 (back), an example of the ozonated test, is shown in Figures 4.17 - 4.19 and SEM photo in Figure 4.20. Sample #5-7 (front) an example of the ozonated coupons, using the flat PTFE washer, is given in Figures 4.21 - 4.23 and SEM photo in Figure 4.24. The Teflon™ washers were inverted for comparative study with the other "flat" polymer washers.

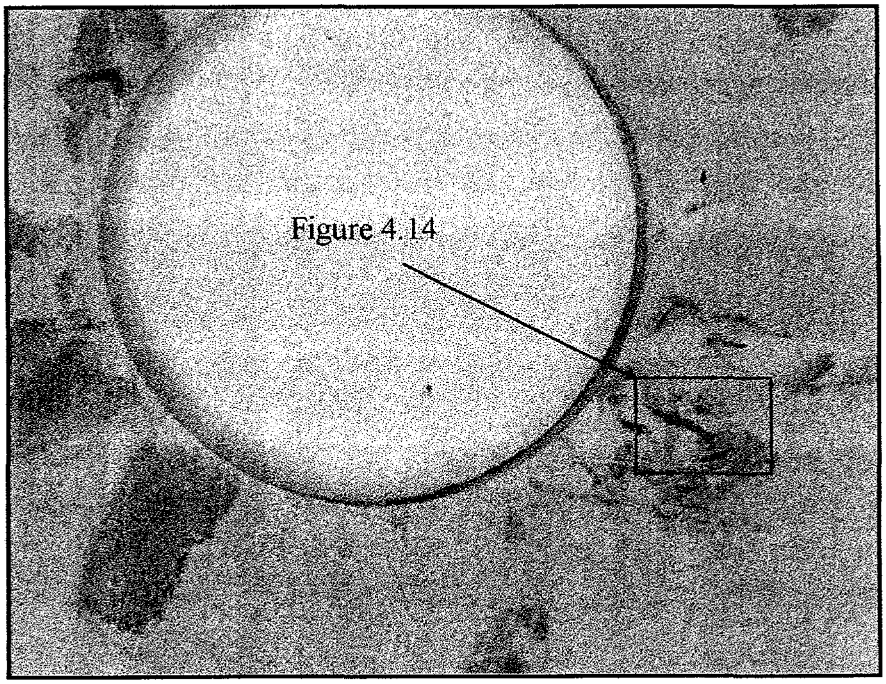


Figure 4.13 Ozonated Saran Sample #4-1 (Back)

Figure 4.14 Ozonated Saran Sample #4-1 (Back). Higher Magnification Photo of Highlighted Area in Figure 4.13.

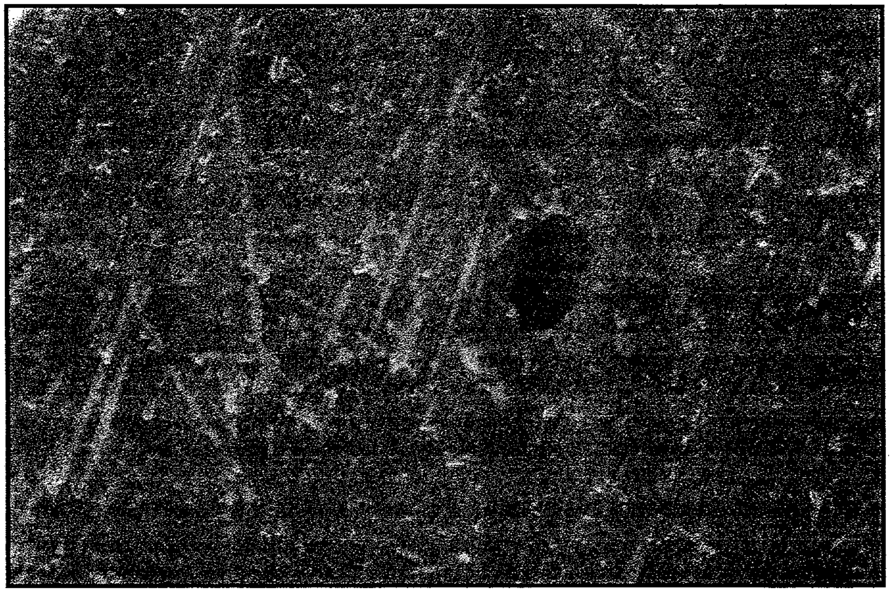


Figure 4.15 SEM Micrograph of Ozonated Saran Sample #4-1 (Back). 292X

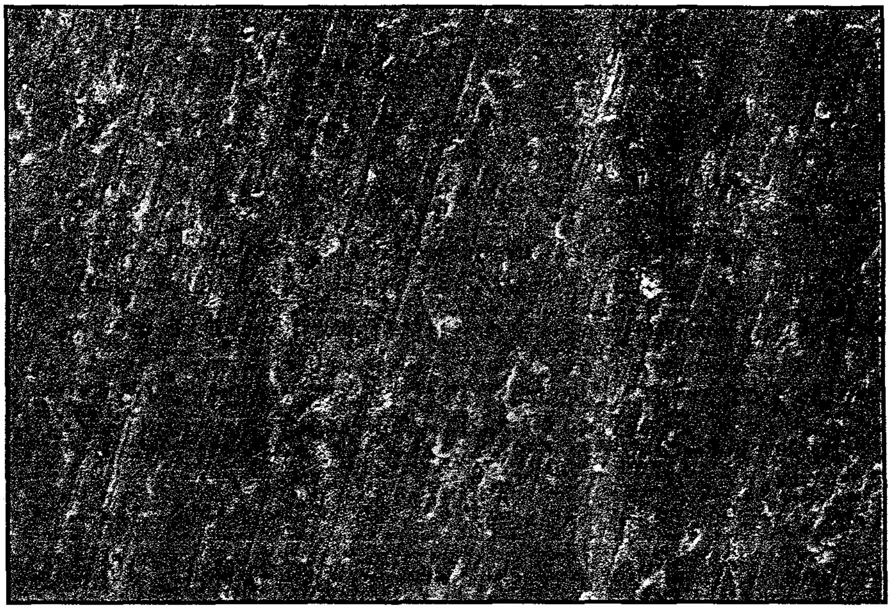


Figure 4.16 SEM Micrograph of Aerated Saran Sample #4-5 (Back). 316X

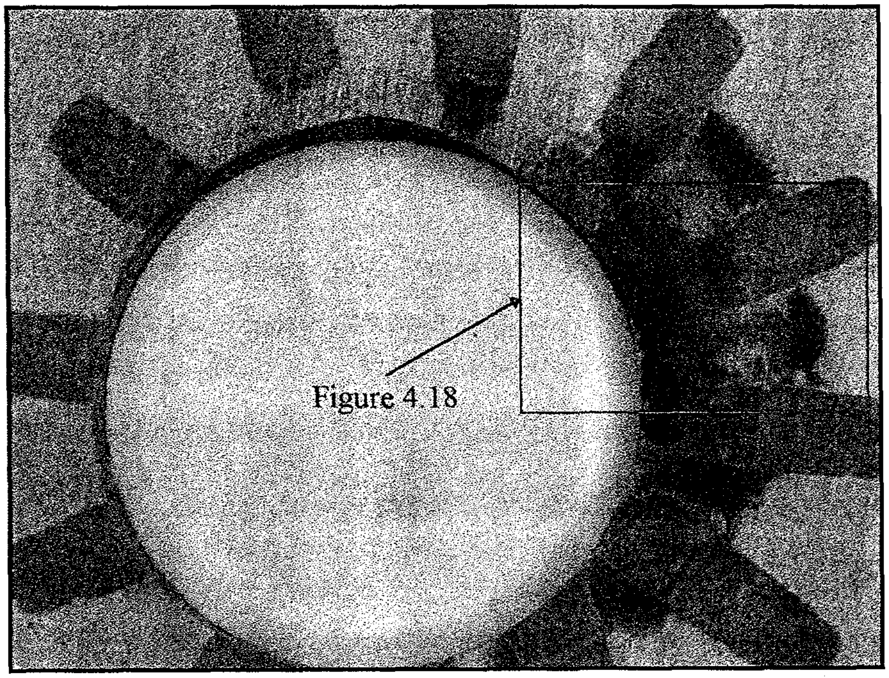


Figure 4.17 Ozonated PTFE Sample #5-8 (Back)

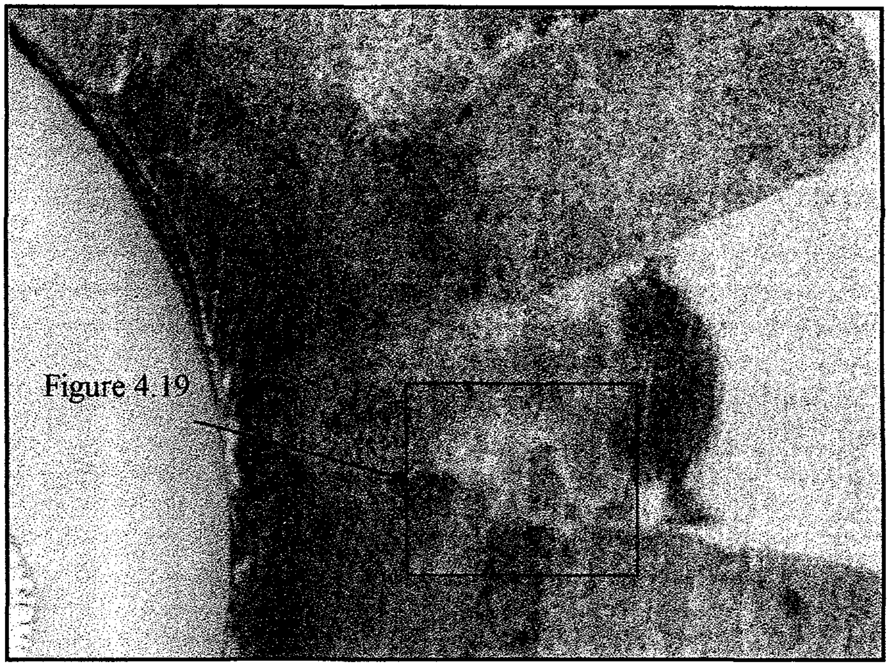


Figure 4.18 Ozonated PTFE Sample # 5-8 (Back). Higher Magnification Photo of Highlighted Area in Figure 4.17.

Figure 4.19 Ozonated PTFE Sample #5-8 (Back). Higher Magnification Photo of Highlighted Area in Figure 4.18.

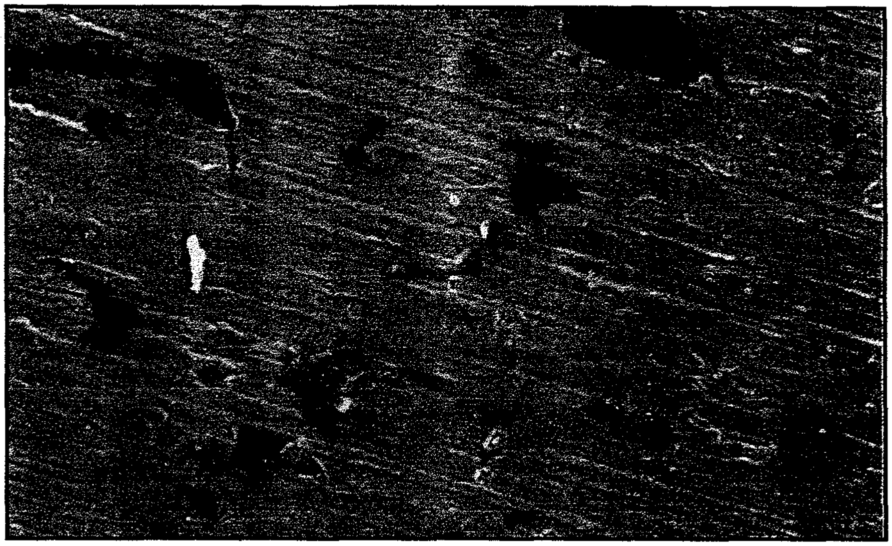


Figure 4.20 SEM Micrograph of Ozonated PTFE Sample #5-8 (Back). Photo of Slot Area 482X.

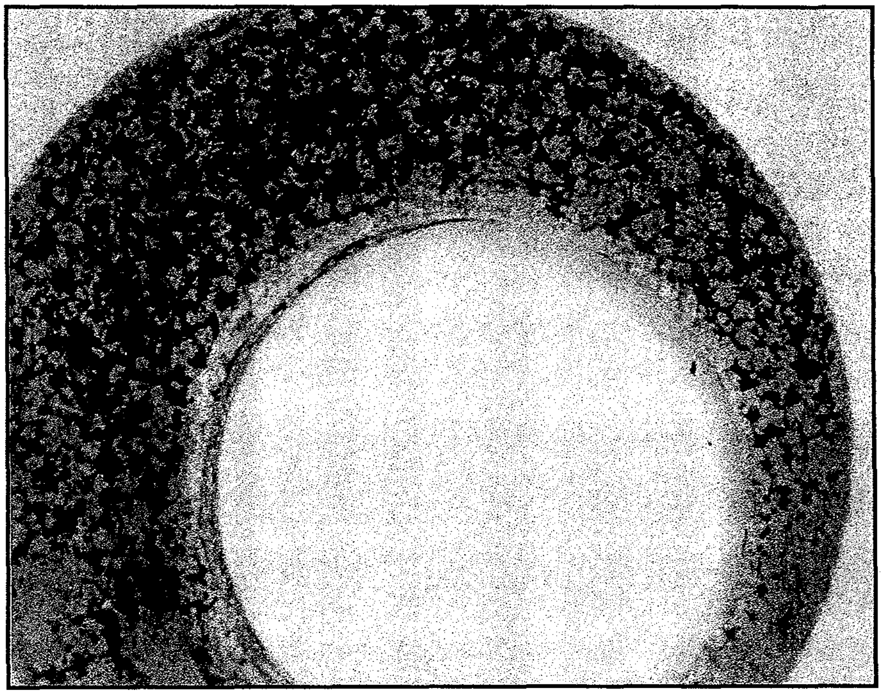


Figure 4.21 Ozonated PTFE Sample #5-7 (Front)

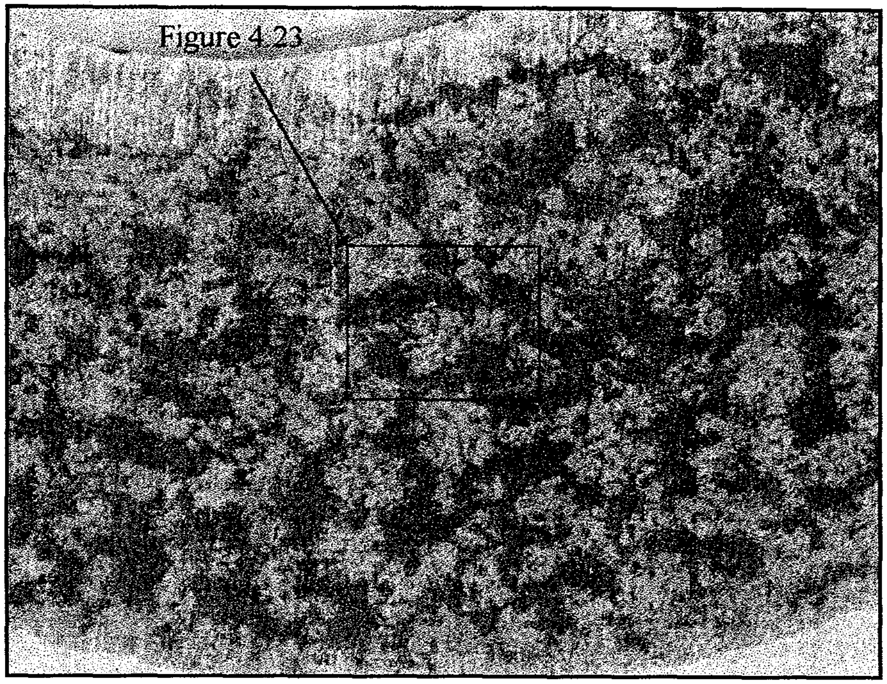


Figure 4.22 Ozonated PTFE Sample #5-7 (Front)

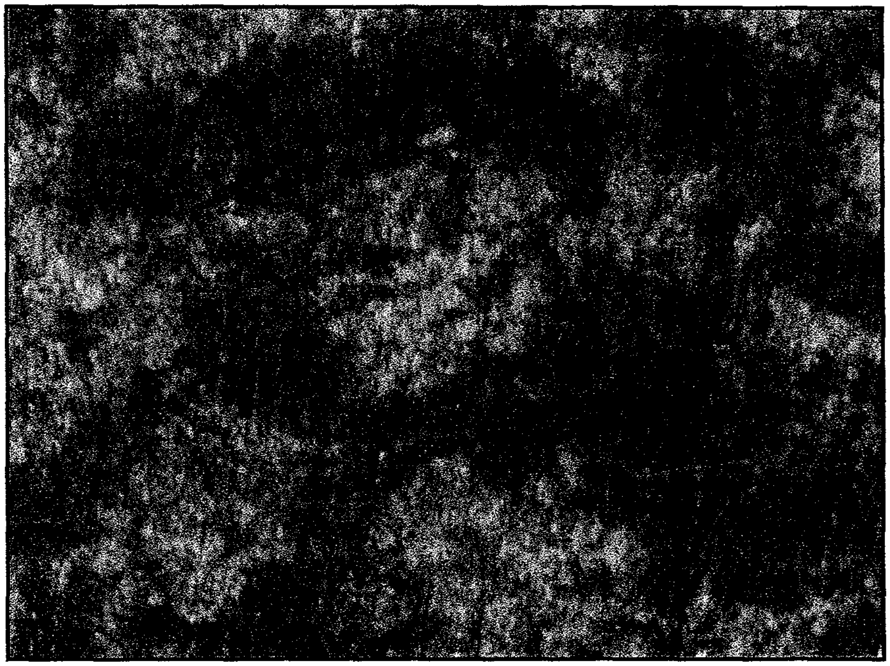


Figure 4.23 Ozonated PTFE Sample #5-7 (Front). Higher Magnification Photo of Highlighted Area in Figure 4.22.

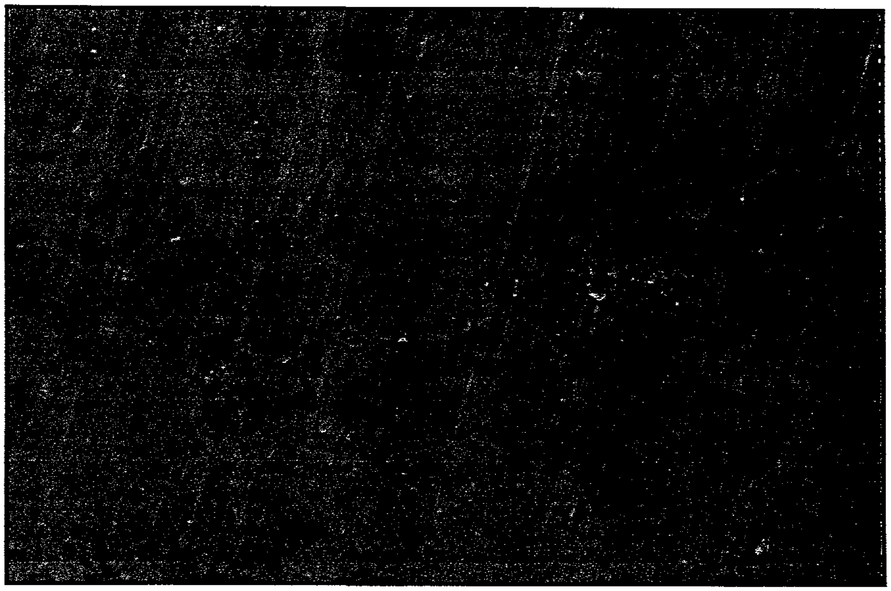


Figure 4.24 SEM Micrograph of Ozonated PTFE Sample #5-7 (Front). 128X

Energy dispersive x-ray (EDS) analysis of the Teflon™ crevice ozonated samples revealed the consistent presence of fluorine on surfaces exhibiting corrosion. Often, in very localized areas, the levels of fluorine appeared to be substantial. Analysis of the titanium surface away from the affected areas showed no sign of fluorine. This evidence confirms the data generated by the previous Rensselaer study.[2]

The results in the aerated tank with the PTFE washers had no macroscopic corrosion, but under low and high magnification SEM analysis, Figures 4.25 and 4.26, a corrosion product was evident. In addition, EDS revealed strong indications of fluorine in the darkened areas along the outer edge of the PTFE flat washer of sample #5-1. Sample #5-2, a crenelated washer, showed similar microscopic effects and exhibited the presence of both fluorine and chlorine in the effected areas.

Since the fluorine levels in the artificial seawater solutions were only 1 PPM, the fluorine found on the corroded surfaces cannot be explained solely on the basis of its initial presence in the bulk solution. The greater possibility is a mechanism whereby the Teflon™ is chemically attacked inside or quite possibly, based on weight loss results, even outside the crevice. Whether UV radiation in the presence of a polymer photosensitizing material, such as titanium oxide, or applied stress to the polymer play pertinent roles in this degradation process remains to be proven and are suggestion for future research.

Figure 4.25 SEM Micrograph of Aerated PTFE Sample #5-1. 14.4X

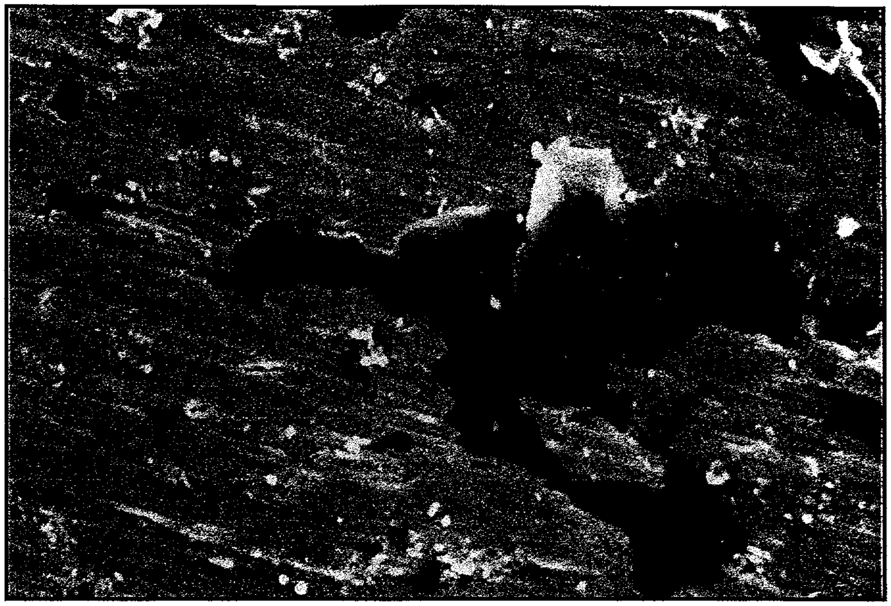


Figure 4.26 SEM Micrograph of Aerated PTFE Sample #5-1 (Front). 1100X

Regardless of the mechanism of fluorine generation, its presence in the crevice is strong evidence that the titanium corroding agent is hydrofluoric acid.

PART 5
DISCUSSION

Except for the PVC samples in the aerated bath, all other weight loss samples lost weight. The aerated PVC samples must be reacting to the seawater environment in a manner which is contributing to their mass rather than removing material from the PVC samples. The weight loss in the PVC under ozonated conditions is most likely due to dehydrochlorination of the polymer (see Section 2.6.4). The PTFE samples lost approximately the same percentage weight in both the aerated and the ozonated seawater solutions. This suggests that ozone does not significantly affect the degradation of PTFE to cause a relevant difference in mass reduction with respect to the aerated condition. The aerated PTFE showed a higher percent weight loss than both the PVC or PEHD under the same conditions. The largest percent weight loss occurred with the PEHD in the ozonated bath. Polyethylene is more susceptible to degradation in an ozonated seawater solution than either PVC or PTFE. The PEHD in the aerated solution was virtually unaffected by the environment.

The titanium corrosion samples showed no signs of corrosion or the presence of chlorine, fluorine or iron. Neither the mechanisms of crevice corrosion or galvanic corrosion were evident for these test samples in either the ozonated or aerated test baths.

The results of the PVC tests indicate the classical crevice corrosion mechanism with chlorine present in the corrosion product. Considering the ozonated seawater environment and the resultant surface bleaching of the PVC dehydrochlorination of the PVC polymer is a likely parallel reaction.

Figures 5.1 and 5.2 show the initiation and propagation stages, respectively, of classical crevice corrosion involving chlorine and two metals.[4] In the case of a polymer and titanium crevice corrosion, one of the metals in the figures would be replaced with PVC. By dehydrochlorination the PVC would be an additional source of chloride ions.

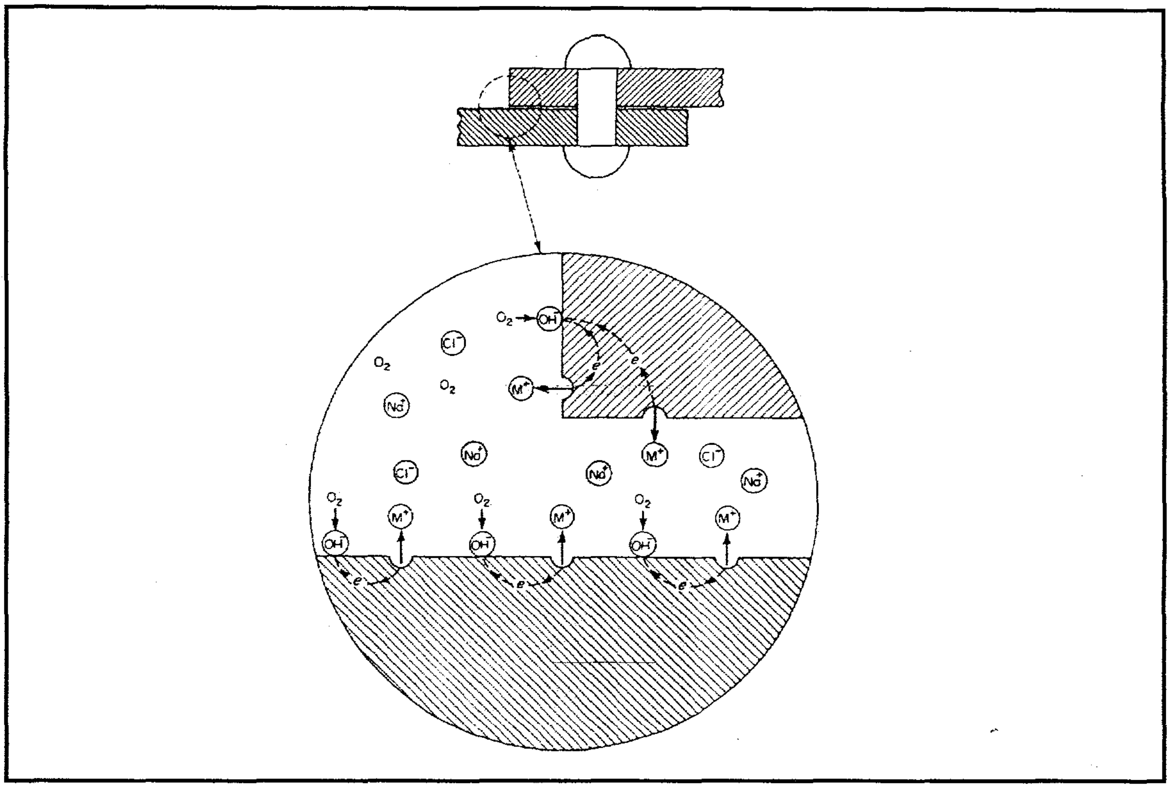


Figure 5.1 The Initiation Stage of Crevice Corrosion

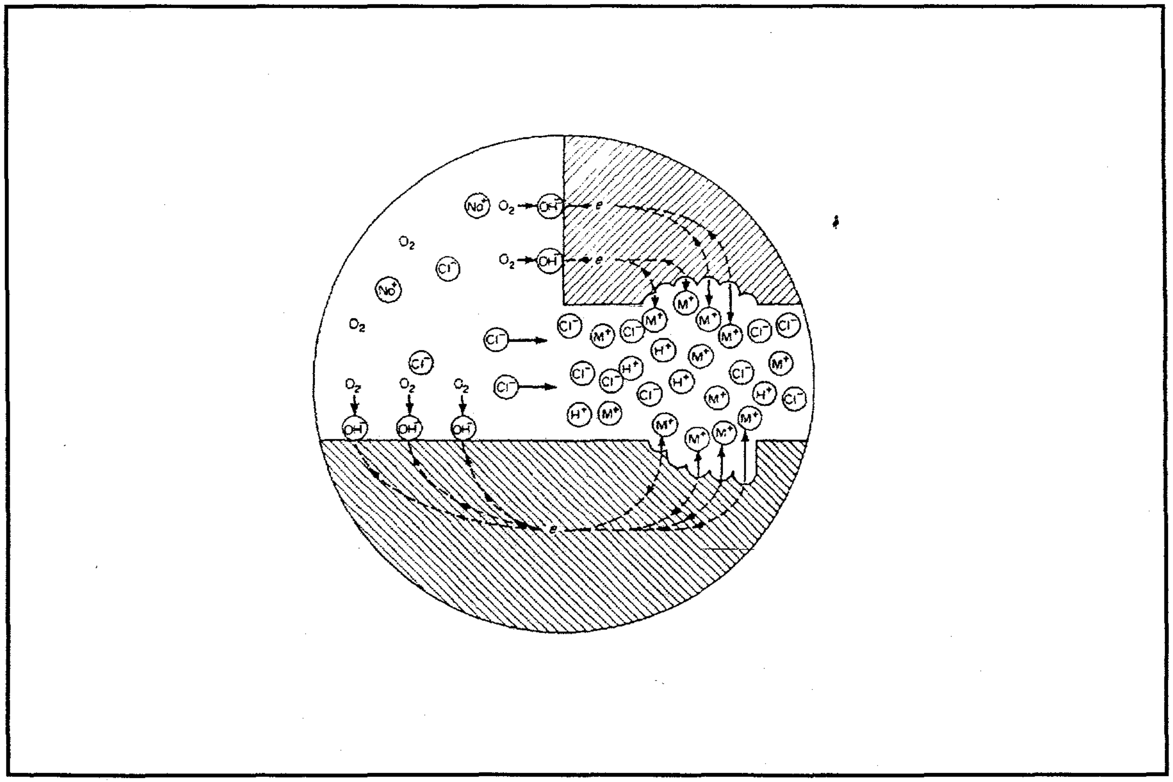


Figure 5.2 The Propagation Stage of Crevice Corrosion

The results of the PEHD corrosion tests were mixed. Chlorine was found in the corrosion product, suggesting the traditional crevice corrosion mechanism similar to the PVC samples, but without the parallel dehydrochlorination reactions. Fluorine was also present in the corrosion product of one of the test samples. Refer to Appendix C for EDS analysis results.

Since only one of the three tested PEHD samples contained fluorine, it might be easier to treat it as an anomaly and dismiss it. However, this should not be done until further testing is completed to verify the results. The following is an attempt at understanding the origin of the fluorine found on the surface of coupon #3-3. Since PEHD does not contain fluorine, its presence on the surface of the titanium coupon can only be accounted for by: (1) contaminants unrelated to the mechanisms of crevice corrosion; or (2) the migration of fluorine into the differential aeration cell (the crevice) from the bulk solution during the corrosion process. It is suggested in this thesis that further research is necessary to reproduce and understand these results.

Saran experienced corrosion results similar to the PVC. Since Saran contains chlorine, crevice corrosion involving the chloride ion is the likely mechanism, occurring in parallel with dehydrochlorination.

The ozonated PTFE corrosion samples experienced visible corrosion product. Fluorine was present in the corrosion product. The crevice corrosion mechanism shown in Figures 5.1 and 5.2 is also applicable here. As with the PVC, one of the metals displayed in the figures would be replaced with PTFE and the chloride ions would be replaced with fluorine ions. Although the aerated PTFE samples showed no macroscopic evidence of corrosion, SEM and EDS analysis of the surface found areas affected by corrosion and the presence of fluorine. Refer to Appendix C for EDS analysis results. It appears that the mechanism for crevice corrosion of titanium and PTFE in seawater is not limited to only ozonated conditions. It can occur in an aerated seawater environments as well.

The occurrence of titanium crevice corrosion in the presence of Teflon™ is not new. Mars Fontana describes a situation of "catastrophic failures of heat exchangers...due to contact with Teflon and a plastic containing lead."[4]

PART 6
CONCLUSIONS

1. The PVC weight loss samples demonstrated an average weight loss of 0.6% in the ozonated seawater solution, while a small net weight gain of 0.05% was observed for the samples in the aerated tank. In addition, the PVC weight loss samples exposed to the ozone experienced a whitening effect. The PEHD samples in the ozonated bath lost slightly more weight than the comparable PVC samples, approximately 1.4%. The PEHD under aeration had an average weight loss of 0.03%. The Teflon™ weight loss was relatively small, approximately 0.025 - 0.03%, under both ozonated and aerated seawater conditions.

2. There was no visual or SEM evidence of corrosion or pitting on the titanium washer crevice samples. Both tests, ozonated and aerated specimen, had similar results. EDS analysis of the ozonated and aerated coupon surfaces found no evidence of fluorine or chlorine. Iron, found on titanium-titanium crevice samples during previous Rensselaer studies, was absent for these test results.

3. The three PVC crevice samples in the ozonated solution had corrosion and surface discoloration. Fluorine was not present on any of the coupon surfaces, but chlorine was found in the affected areas. The aerated counterparts had no indication of crevice corrosion or surface effects, and corrosion product was not present under EDS analysis. The outer circumference of the PVC washer in the ozone bath demonstrated a whitening effect similar to the PVC weight loss samples, but the whitening in the crevice test was much more pronounced. This surface whitening is probably the result of dehydrochlorination of the PVC. The ozonated PEHD samples also showed signs of corrosion, while the aerated ones had no surface discoloration. Of the three ozonated samples, only one had evidence of chlorine and another had signs of fluorine. There was no corrosion product, chlorine or fluorine found on the aerated PEHD samples which were analyzed using SEM and EDS. The results for the Saran crevice test were similar

to the PVC tests. In the ozonated tank the Saran corrosion samples had isolated signs of discoloration. EDS analysis was not able to find corrosion product, but classical crevice corrosion is strongly suspected. In the aerated tank the samples had no indications of corrosion and again no corrosion products were found on the surface.

4. The Teflon™ ozonated crevice samples all showed signs of corrosion, pitting, and the presence of fluorine. These ozonated solution results were consistent for both the crenelated surfaces and the flat PTFE surfaces in contact with the titanium coupon. The aerated Teflon™ crevice samples did not demonstrate visible signs of corrosion. They did show microscopic corrosion, the presence of fluorine under EDS analysis and a limited degree of pitting for both the crenelated and the flat surface washers. The extent and severity of corrosion of the aerated samples was minimal relative to the ozonated test samples. The presence of crevice corrosion and fluorine on the ozonated titanium coupons supports the results of the previous Rensselaer studies performed by Brown, Wyllie and Duquette. Since fluorine is the only possible corrosive agent found exclusively in the effected areas, it is concluded that fluorine is the major contributing factor to the crevice corrosion of grade-2 titanium in both ozonated and aerated artificial seawater using Teflon™ generated crevices.

5. The general mechanism for the crevice corrosion of titanium with Teflon™ at room temperature, appears to be dependent on the deterioration of the Teflon™. Breakdown of the PTFE provides sufficient fluorine ions in a tight aeration cell environment to produce corrosive hydrofluoric acid. The specific mechanisms explaining these interactions which ultimately lead to the corrosion and deterioration of titanium are not known, but it is highly probable that the mechanism is similar to the classical crevice corrosion involving chloride ions, refer to Figures 5.1 and 5.2.

Fluorine was also found in the corrosion product of one of the PEHD samples under ozonation conditions. If this result, limited to only one sample, is valid and not an anomaly based on contaminants, it is reasonable to assume that the fluoride ions migrated into the crevice. The ion flux was probably in a manner similar to the migration of the chloride ions into a differential aeration cell in the more conventional crevice corrosion process. Leaving the exact mechanism for future inquiry, the results of this study confirm the production of crevice corrosion on titanium in artificial seawater in Teflon™ generated crevice environments.

PART 7
SUGGESTIONS FOR FUTURE RESEARCH

In an attempt to better understand the mechanism and the extent of damage due to Teflon™ based crevice corrosion of titanium based alloys, additional research is required. The following is a list of suggested areas for continued study in this field.

6.1 The effects of ozone on Teflon™ in seawater are not entirely understood, especially under increased stress conditions. An understanding of the mechanism by which Teflon™ degrades in ozonated and aerated seawater is needed. Tests should be designed to determine the effects, if any, an applied stress may have on Teflon™ degradation in various seawater environments. Related to these tests, the determination as to whether the degree of crevice corrosion is directly correlated to the stress applied to the PTFE samples. These results should be compared to data generated from similar tests under aerated conditions.

6.2 It is assumed that the by-product of the leaching fluorine is hydrofluoric acid, one of the few chemicals known to etch the resilient titanium oxide surface of titanium. Experiments should be designed to monitor the chemistry inside the crevice to determine directly, rather than by EDS or WDS analysis, concentration levels of hydrofluoric acid. Analysis should provide the determination of the onset of hydrofluoric acid.

6.3 The extent of damage to parts and equipment manufactured with titanium based alloys and the possibility of failure must be understood if ozone is to be a viable defouling product. It will be important to determine whether the results of this study are significant. Even without the understanding of specific mechanisms underlying this corrosion process, corrosion rates under varying conditions must be studied and understood. Temperature effects, ultraviolet light effects on Teflon™ and/or titanium oxides, the degree of titanium alloying, sea water solution concentration, and the degree of stress are all variables worth consideration. If future tests determine that crevice corrosion under specific conditions pose a threat to the serviceability of equipment then alternative materials and/or environments will have to be employed.

6.4 Tests should be designed to determine the source of the fluorine in non-Teflon™ crevice fixtures. If it is determined that the source is not accidental contamination and the fluorine does come from the bulk solution, then additional tests will be needed. The fluorine concentration in the bulk solution required to cause migration into the differential aeration cell in sufficient quantities to damage to the titanium surface should also be determined.

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APPENDIX A
ADDITIONAL RESULTS

Although not part of the scientific controls of this study a few interesting occurrences are worth noting.

In the ozonated seawater solution that the grade-2 titanium washers in test group #5 (PTFE) demonstrated similar corrosion behavior at locations where they contacted the Teflon™ washers. The flat PTFE washer imprint is visible as a ring of corrosion. Figure A.1 is a photograph of a titanium fixturing washer that was in contact with the flat side of a PTFE washer. Not only did the fixturing titanium washers corrode when in contact with the Teflon™ washer, but some titanium washers also had corrosion product when in contact with the Teflon™ tape. Figure A.2 is a photo of such a washer. Notice the distinct coloration and the corroded outline of the fixturing nut.

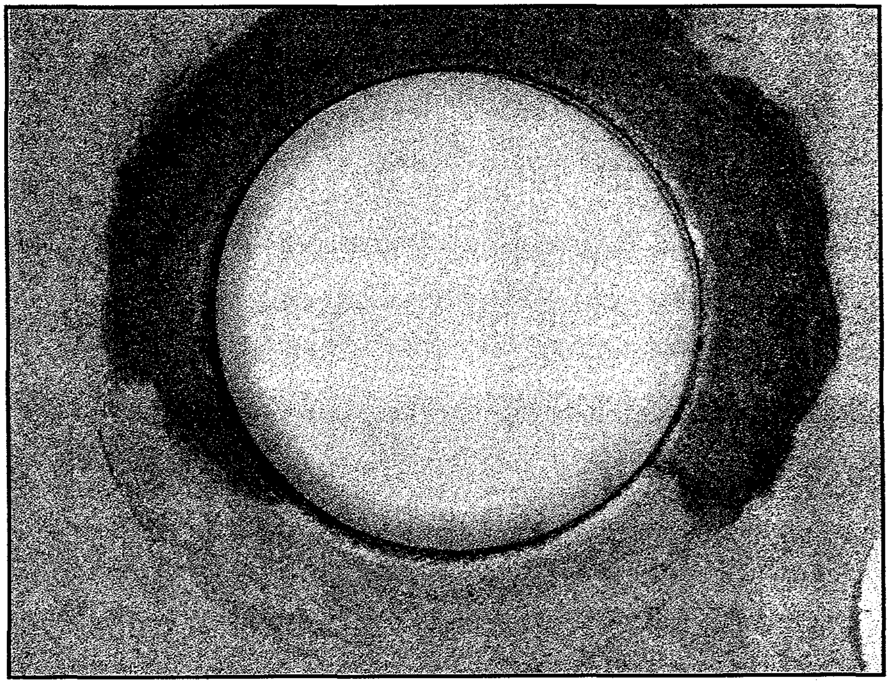

Figure A.1 Ozonated PTFE Flat Washer on Ti Washer

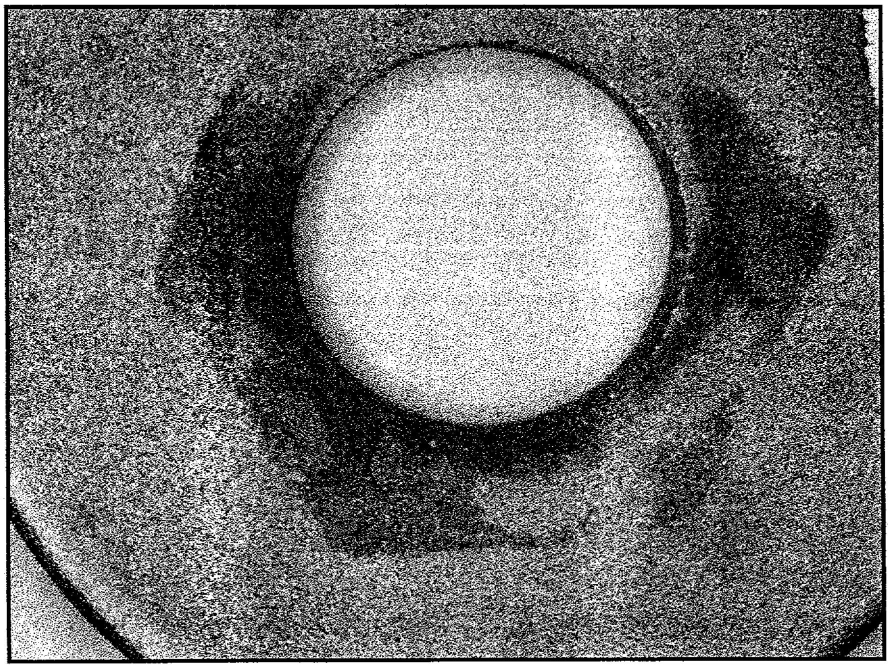

Figure A.2 Ozonated. Corrosion Impression of Fixturing Nut on Ti Washer Due to Teflon™ Tape.

APPENDIX B
TITRATIONS

Hypohalite and Bromate Titration

Hypohalite and Bromate Titration

Modified from: Haag, W. R. *Technical Note on the Disappearance of Chlorine in seawater*. Water Research, Vol. 15, 1981. p 937.
Modified by: Gordan Grguric, 1991, Barbara Brown, 1995.

Reagents:

1. **0.3 M Potassium Iodide.** Dissolved 25 g of potassium iodide in 500 mL of distilled deionized water. Store in a dark bottle to prevent photo-oxidation of the iodide. Discard the solution when it becomes faintly yellow.

2. **Ammonium Molybdate Catalyst.** Dissolve 7.5 g of ammonium molybdate in 250 mL distilled deionized water.

3. **pH 3.8 Acetate Buffer.** Dissolve 31.23 g of hydrated sodium acetate $CH_3COONa \bullet 3H_20$ and 120 g (114 mL) of glacial acetic acid in 250 mL of distilled deionized water.

4. **9 N Sulfuric Acid.** Fill a 500 mL volumetric flask half-full with distilled deionized water. Carefully add 125 mL concentrated sulfuric acid . Fill to the 500 mL mark with distilled deionized water. Mix well and let the flask cool to room temperature (use water and ice bath, if necessary). When cooled, fill to the mark again.

5. **Starch Solution (indicator).** Dissolve 2 g of soluble starch in 200 mL of distilled-deionized water. Heat the solution to boiling. After letting it cool to room temperature, filter the solution and use only the clear filtrate. This solution is stable for 1-2 weeks and can be preserved with 1 mL of phenol.

6. **Potassium Bromate Standard.** Analytical grade potassium bromate is dried at 180°C for several hours. After cooling in a desiccator overnight, weigh exactly 16.70 g and dissolve in 1 L of distilled deionized water. This is your 0.1 M bromate standard.

7. **Sodium Thiosulfate Titrant.** Prepare 0.01 M sodium thiosulfate by dissolving cca.1.24 g hydrated sodium thiosulfate in 500 mL of distilled deionized water. Store in a dark bottle. It can be preserved with 0.5 mL of amyl alcohol. Alternately, 0.01 M sodium thiosulfate can be prepared by diluting standard 0.1 N (=0.1 M) sodium thiosulfate stock solution, if available.

Standardizing the Sodium Thiosulfate Solutions:

1. Pipet 20 mL of distilled deionized water in a 50 mL Erlenmeyer flask. Add exactly 0.1 mL of potassium bromate standard solution.

2. While stirring, add the following reagents in succession: 1 mL of potassium iodide, 0.1 mL of ammonium molybdate, 1 mL of 9 N sulfuric acid, and 1 mL of the starch solution.

3. Titrate this solution with sodium thiosulfate until the blue color completely disappears. You will need approximately 6 mL of the titrant to reach the endpoint.

4. Calculate the molarity of the thiosulfate solution from the equation:

$$M(Na_2S_2O_3)=0.06/V(Na_2S_20_3 \text{ used, in mL})$$

Procedure

A. Hypohalite Titration:

1. Place a stir bar in a 50 mL Erlenmeyer flask. Pipet exactly 20 mL of the sample into a 50 mL Erlenmeyer flask.

2. While stirring, add the following reagents in succession: 1 mL of potassium iodide, 0.1 mL of ammonium molybdate, 1 mL of pH 3.8 acetate buffer and 1 mL of the starch indicator. If there is hypochlorite or hypobromite present, the solution will turn blue. Titrate with your standardized sodium thiosulfate until the blue color completely disappears. Make certain you do not overshoot this endpoint as the same titration is continued at pH 1 to determine the bromate concentration in the sample. If you overshoot the first endpoint you will have to redo the hypohalites titration.

3. Calculate the concentration of hypehalites (hypobromite and hypochlorite) using the equation:

$$mM(\text{hypohalites}) = 25{,}000 * V(Na_2S_2O_3) * M(Na_2S_2O_3)$$

Where: $V(Na_2S_2O_3)$ is the volume of titrant used, in mL
$M(Na_2S_2O_3)$ is the molarity of sodium thiosulfate

B. **Bromate titration:**

1. To the sample just titrated, add 1 mL of the 9 N sulfuric acid. The blue color will reappear if there is bromate present. Titrate with sodium thiosulfate again until the blue color disappears.

2. The bromate concentration is calculated from the equation:

$$mM(BrO_3^-) = V(Na_2S_2O_3) * M(Na_2S_2O_3)/120{,}000$$

Where: $V(Na_2S_2O_3)$ is the volume of titrant used, in mL
$M(Na_2S_2O_3)$ is the molarity of sodium thiosulfate

Bromide Titration

Bromide Titration

Modified from: K. Grasshoff, *Methods of Seawater Analysis*, NY, Verlag Chemie, 1976.
Modified by: Gordan Grguric, 1991; Barbara Brown, 1995.

Reagents:

1. **Sodium Chloride Solution.** NaCl 10% (w/v). Dissolve 50 g of NaCl in 500 mL of distilled water.

2. **Phosphate Buffer.** $NaH_2PO_4 \bullet H_2O$. Dissolve 25 g of sodium dihydrogen phosphate (sodium phosphate monohydrate) in 250 mL of distilled, deionized water and dilute to 500 mL.

3. **Sodium Hypochlorite Solution.** NaOCl. Prepare a 0.1 N solution of NaOH by adding 1 g of NaOH in 250 mL of distilled, deionized water. Fill a 250 mL flask with 70 mL of 4-6% sodium hypochlorite solution. To this flask add 30 mL of 0.1 N NaOH solution.

4. **Sodium Formate Solution.** Dissolve 50 g HCOONa, Sodium Formate, to 85 mL of distilled, deionized water.

5. **Potassium Iodide Solution.** SAME AS HYPOHALITE and BROMATE TITRATION.

6. **Ammonium Molybdate Catalyst.** SAME AS HYPOHALITE and BROMATE TITRATION.

7. **6 N Sulfuric Acid.** H_2SO_4. Fill a 1 L flask with 330 mL of 9 N sulfuric acid solution (from hypohalite and bromate titration). Add 170 mL of distilled, deionized water.

8. **Starch Solution (Indicator).** SAME AS HYPOHALITE and BROMATE TITRATION.

9. **0.01 M Sodium Thiosulfate (Titrant).** SAME AS HYPOHALITE and BROMATE TITRATION.

Procedure

Bromide Titration:

1. Pipet 10 mL of seawater into a 250 mL flask. Add the following reagents in succession: 10 mL of sodium chloride, 10 mL of phosphate buffer, and 2 mL of hypochlorite solution.

2. Heat solution on a hot plate for approximately 6 minutes at a setting of 4 on the Corning® hot plate. The solution will turn from clear to opaque. Carefully add 5 mL of sodium formate solution while stirring. Cool to room temperature.

3. Add the following reagents in succession: 5 mL of potassium iodide, 0.2 mL molybdate solution, 10 mL of 6 N sulfuric and 10 mL of starch indicator. Start titration after 30 seconds with sodium thiosulfate until solution is colorless.

4. Calculate the concentration of bromide using the equation:

$$\mathrm{mM(Br^-)} = V(\mathrm{Na_2S_2O_3}) * M(\mathrm{Na_2S_2O_3}) * 16667$$

Where: $V(\mathrm{Na_2S_2O_3})$ is the volume of titrant used, in mL
$M(\mathrm{Na_2S_2O_3})$ is the molarity of sodium thiosulfate

APPENDIX C
EDS Analysis

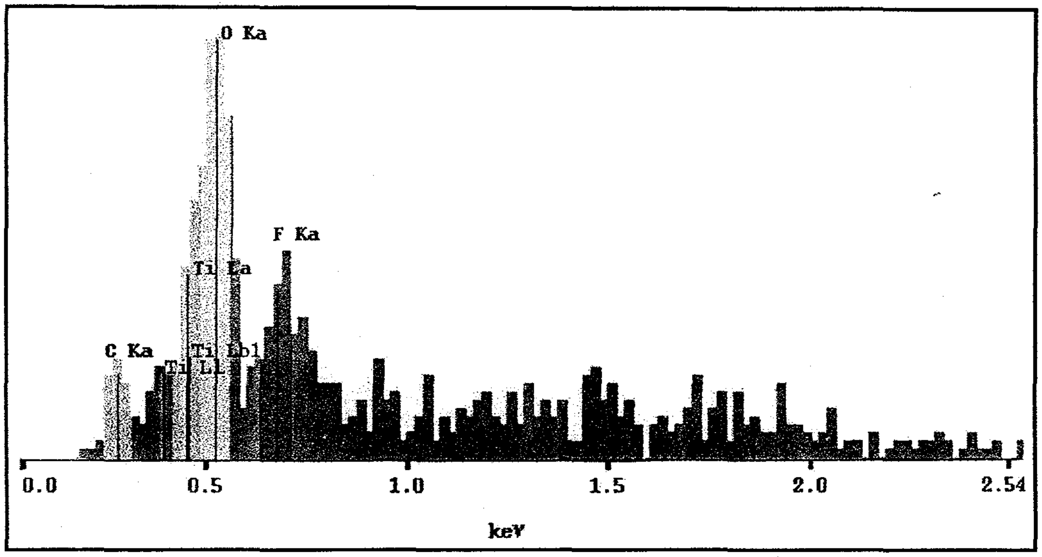

Figure C.1 EDS Analysis of PEHD Corrosion Coupon #3-3 in Ozonated Seawater Solution

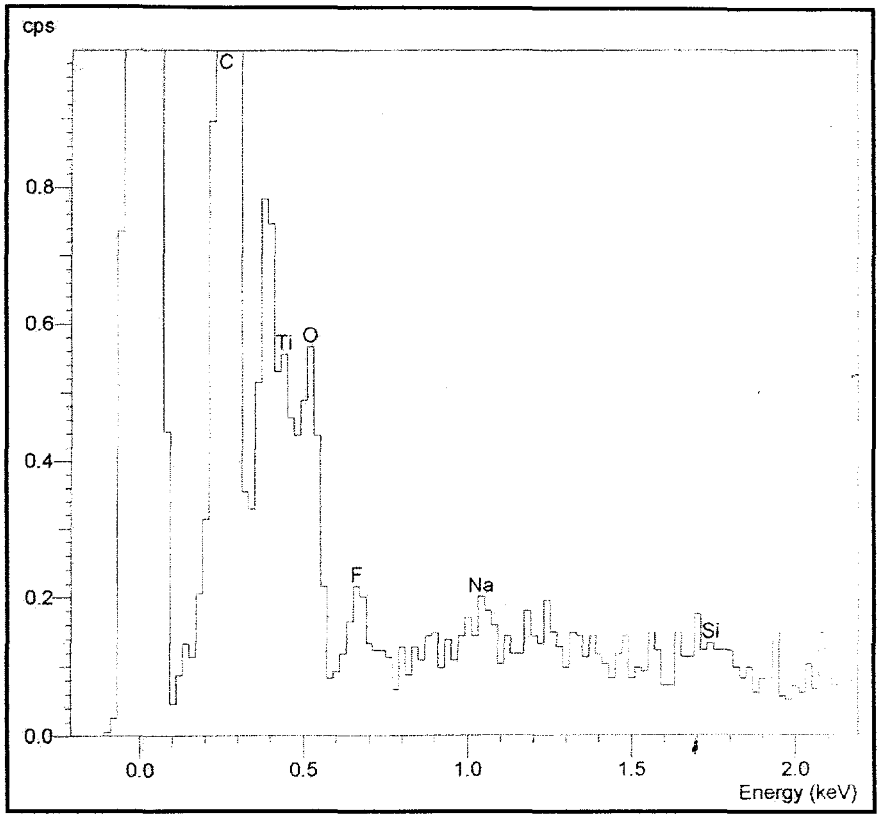

Figure C.2 EDS Analysis of PTFE Corrosion Coupon #5-2 in Aerated Seawater Solution