

# Behavior of Materials in a Subsurface Ocean Environment

L. A. BEAUBIEN, I. WOLOCK, AND C. L. BUCHANAN

*Ocean Technology Division  
Naval Research Laboratory*

and

C. L. WHITMAN

*Naval Ordnance Station  
Indian Head, Maryland*

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## ABSTRACT

Information is presented on the deterioration in sea water of materials and undersea-system components, based on published and unpublished studies, and on authoritative opinions. The items chosen for evaluation are primarily those likely to be used in deep-ocean structure and systems. Materials included are metals, plastics and composites, ceramics, paper, natural fibers; components included are photographic materials, magnetic tape, electronic components, and propellants and explosives. Marine corrosion of metals is represented in the form of an annotated bibliography; the remaining entries consist of summaries of material and component behavior coupled with pertinent bibliographies. The form and scope of these summaries run from comprehensive evaluations in the areas of plastics and propellants to relatively brief opinions of authorities for items of lesser marine utility or occurrence.

## PROBLEM STATUS

This is a final report on one phase of the NRL Problem.

## AUTHORIZATION

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## BEHAVIOR OF MATERIALS IN A SUBSURFACE OCEAN ENVIRONMENT

### BACKGROUND AND GENERAL INTRODUCTION

As tasks become more varied at greater depths in the oceans, a larger spectrum of materials and components with differing areas of utility is required. Unfortunately many materials deteriorate to some extent when immersed for extended times in seawater. Although such deterioration has long been recognized for many presently used or candidate materials, in many cases relatively little work has been done to determine its actual nature and extent. Even for materials reasonably well studied, it is often difficult for a designer to locate the available information or to put differing, or even contradictory, opinions into perspective. Two extensive symposia have been held on the performance of materials in a marine environment, and the resulting papers published.\* However, these papers were not intended to serve as comprehensive reviews on deterioration, and they were limited primarily to structural materials.

The present project was undertaken to determine the actual state of knowledge of the effect of seawater on a large class of materials and components, by uncovering and assembling all available information. The choice of materials to be covered was dictated by interest in structures or systems intended either to be placed on the ocean floor or to be moored fully submerged and by interest in marine rescue and salvage operations. Hence materials which are primarily associated with shoreline facilities, such as wood and concrete, are not included. Likewise, the topic of marine fouling itself, as distinct from the possible damage to materials by the fouling organisms, is not covered.†

The principal sources of information were the Defense Documentation Center, Oceanic Library and Information Exchange, and the abstracts compiled between 1945 and 1964 by the now defunct Prevention of Deterioration Center. These were augmented by searches through the Atomic Energy Commission Abstracts, the Department of Commerce Index to Federal Research and Development Reports, and pertinent technical journals. In some cases authorities were contacted for additional information.

The results of this survey are presented here in five essentially independent sections: a critical review of effects of seawater on polymeric materials and composites; a review of the effects of seawater on ceramics, paper, fabrics, film, and magnetic tape; a review and a bibliography on the effects of seawater and hydrostatic pressure on electronic components; an annotated bibliography on marine corrosion of metals; and a report on the effects of seawater on propellants and explosives (prepared by the Naval Ordnance Station, Indian Head, Maryland).

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\*Ocean Engineering, Vol. 1, Nos. 2, 3, and 4 (1968-1968); "Materials Performance and the Deep Sea," ASTM Special Technical Publication 445, Phila., Pa., American Society for Testing and Materials, 1969.

† For information on the related subjects of marine deterioration of wood and biological fouling, the following references are suggested: "Marine Borers, an Annotated Bibliography," W.F. Clapp and D.R. Kenk, ONR Report ACR-74, 1963; "Marine Borers, Fungi, and Fouling Organisms," E.K.G. Jorns and S.K. Eltringham, editors, Organization for Economic Cooperation and Development, Paris, 1971; "Marine Fouling and Its Prevention," Woods Hole Oceanographic Institute, U.S. Naval Institute, 1952.

## POLYMERIC MATERIALS AND COMPOSITES

I. Wolock  
Ocean Materials Criteria Branch  
Ocean Technology Division, NRL

### POLYMERIC MATERIALS

There has been great interest in polymeric materials for applications in the ocean such as submarine telephone cable coverings, mooring lines, seals and gaskets, and various structural components. These materials combine good electrical properties with good resistance to general deterioration and corrosion in water. Furthermore the materials resist marine biological attack. To evaluate this behavior characteristic and to obtain general information on the behavior of polymeric materials in the ocean environment, a number of ocean exposures have been conducted for extended times.

Workers at the Bell Laboratories have reported the results of exposures of up to 15 years at Wrightsville Beach, North Carolina, and Daytona Beach, Florida, at respective depths of 3 feet and 5 feet. The sites were selected because of the relatively high level and diversified types of marine borer activity. Seven large-scale exposure tests have been conducted for up to 3 years by the Naval Civil Engineering Laboratory at two locations off the coast of California at respective depths of approximately 2300 feet and 5600 feet deep. The Naval Civil Engineering Laboratory also conducted exposures for the Naval Air Development Center at the two locations for up to 2 years, in addition to one exposure in 35 feet of water in the Port Hueneme, California, area for 1 year. The Naval Applied Science Laboratory conducted an exposure at a depth of 4200 feet in the Tongue of the Ocean, Bahamas, for 1 year.

#### Plastics

Connolly [1],\* Connolly et al. [2], and Muraoka [3-10], and others [11-16] have reported on extensive exposure tests of a large number of plastic materials. The materials included in these exposures are listed in Table 1.

As was pointed out, these exposures were conducted in different locations, at different depths, and at different times. Every material exposed by Muraoka and almost every material exposed by Connolly gave some indication of borer attack in at least one exposure. In most cases, however, the attack was limited to surface indentations up to 1/8 inch in diameter and 1/16 inch deep. In some cases Connolly observed borer damage early in the exposure period, with no additional damage during several years of additional exposure. In some cases Muraoka observed borer damage on a plastic specimen at the area of contact with the sediment on the ocean bottom, but there was no damage 1 or 2 feet above the bottom. In other cases damage was observed only under or in the vicinity of the wood bait in contact with the specimen, and in still other cases damage was observed only under a piece of jute-tape wrapping which enabled the borer to get a start in penetrating the specimen. In some cases, borers attacked a given material during one exposure but not during other exposures at different times at the same approximate location. Thus, like many other natural processes, borer attack was unpredictable.

Although borer attack on plastics was usually restricted to rather shallow surface damage, Connolly et al. [2] reported instances of substantive borer penetration, as deep as 3/4 inch. Two plasticized poly(vinyl chloride) plastics, one with trioctyl phosphate and the other with a nitrile rubber-polyester, "were heavily penetrated by borers and lost their mechanical integrity." Two specimens of nylon pipe were penetrated by borers during the first year of

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\*These references are listed at the end of this section on polymeric materials and composites.

Table 1  
Reported Exposure Tests of Plastics

Material	References
Acrylonitrile-butadiene-styrene	1, 2
Cellulose acetate	3-9
Cellulose acetate butyrate	7, 11
Chlorinated polyether	1, 2
Epoxy	1, 2
Ethyl cellulose	5, 9
Fluorinated ethylene-propylene	3-8
Nylon	1-9
Polyacetal	1-9
Polycarbonate	1-9, 12
Polyester	1, 2
Polyethylene	1-9
Poly(ethylene-ethyl acrylate) copolymer	2
Polyethylene terephthalate	1
Poly(methyl methacrylate) (acrylic)	3-9, 13-16
Poly(monochlorotrifluoroethylene)	1, 2
Polypropylene	1-4, 6-9
Polystyrene	1, 3-9
Polytetrafluoroethylene	1-10
Poly(vinyl chloride)	1-9, 11
Poly(vinylidene chloride)	3, 10

exposure, but there was no additional damage during the next 9 years. A silica-filled styrene polyester casting suffered borer penetration after 6 years of exposure but none additional for the next 7 years, and an epoxy resin cast rod suffered a sufficient number of borer attacks so as to reduce its mechanical strength.

A number of factors would appear to influence the extent of borer damage of plastic materials. Penetration of plastics by borers may be aided by their starting in materials such as wood or jute wrapping or becoming established in heavy irregular calcareous fouling and then penetrating into the adjacent plastic material. Connolly [1] stated that borer attack appears to be directly related to the character of the surface. Generally, waxy or smooth materials such as polyethylene and polypropylene did not show penetration, although there were exceptions.

Muraoka [4] attributed failure of borers to penetrate into plastic materials to four causes: a hard surface; a waxlike surface; a soft, flexible smooth surface; and thick bacterial slime growth, which interfered with the borer getting a start. Connolly reported a pholad entry into a silica-filled polyester casting, which was surprising in view of the extremely hard nature of the formula and the fact that it contains silica. He stated that one theory suggests that pholads may be able to burrow into materials harder than their shells of aragonite because the materials are often friable and the harder grains that are broken off serve as an abrasive at the point of the burrowing.

Bultman and Southwell [11] investigated the effect of material hardness on the susceptibility of poly(vinyl chloride) to borer attack. Several PVC plastics were formulated in which the hardness was varied systematically by the amount of plasticizer in the formulations or by addition of inert fillers. The harder PVC plastics were just as heavily attacked by both teredos and pholads as the softer ones. In addition, cellulose acetate butyrate which had a surface hardness comparable to the PVC formulation with no plasticizer was attacked more severely than the softer experimental formulations. The authors postulated that the less-yielding nature of the harder materials facilitated removal of shavings from the surface by the boring organisms and that these shavings were less likely to clog the denticulated ridges of the shell so that the rasping action could proceed more efficiently.

Pomerat and Weiss [17] studied the collection of sedentary populations on the surfaces of submerged samples of 40 different construction materials. The five plastics exposed were low in the relative amount of fouling accumulated. The results obtained suggested that smooth, nonporous, nonfibrous surfaces, especially if also hard, are poor accumulators of sedentary organisms.

The more severe damage reported by Connolly [1] as compared with the superficial damage reported by Muraoka [3-9] may be due to the exposure locations. Connolly et al. [2] pointed out that "since the environment is biologically more aggressive in shallow water than in deep water, the findings from this program represent the worst situation that could be encountered." The average water temperatures at Wrightsville Beach and Daytona Beach were 17.3°C and 21.9°C respectively, whereas they were 2.5°C and 5.0°C at the two Pacific locations used by Muraoka. This alone could have resulted in greater borer activity at the sites used by Connolly.

The influence on the extent of borer activity of location and the time at which the exposure is taking place would appear to be evident from Muraoka's work. He reported similar behavior for a large group of plastics exposed at the same time, but this behavior varied from one exposure to another at the same location.

In most cases the plastics were not attacked by marine microorganisms. However, some poly(vinyl chloride) plastics containing lead stabilizers have become blackened by sulfate-reducing anaerobic bacteria. These microorganisms as a result of their utilization of the organic material, produce hydrogen sulfide which reacts with the lead compounds, turning the plastic black. However, there is no indication that this discoloration affects the properties of the plastic.

Bultman and Southwell [11] exposed various experimental polymeric materials, otherwise suitable for marine electric cable insulation, for 6 months to 14 months in the Pacific Ocean at Naos Island, Canal Zone, and in the Carribean at Coco Solo, Canal Zone. Twenty-five candidate formulations containing poly(vinyl chloride) resin were prepared, incorporating in various combinations three plasticizers, three toxicants, and a wide variety of inert fillers. Commercial cellulose acetate butyrate was also included. The presence of inert fillers or toxicants or a change in plastic hardness in the PVC formulations had little effect on the amount of pholad damage. However, the PVC formulations containing the inert, inorganic fillers and those containing the toxicants were relatively free of damage by the teredos. Plastic hardness had little effect in this case also.

Connolly et al. [2] observed that two high-density polyethylene materials cracked at the points where they were fastened to the racks after 6 years. This phenomenon is exhibited by some polyethylenes and is not attributed to biological causes. In addition, by infrared analysis, Connolly et al. [2] detected carbonyl groups in unprotected polyethylene rods exposed 13 to 14 years, indicating that this material can oxidize slowly in shallow water where oxygen content is higher than at great depths. Thus some types of deterioration may be encountered during extended underwater exposure which are not biological in origin.

Yoshida et al. [18] also found that polyethylene degrades in water due to oxidation, caused by oxygen dissolved in the water. Once oxidation begins and chain scission occurs in the polyethylene materials, cracks grow in the polyethylene due to environmental stress cracking caused by the water. In addition, if polyethylene insulation is in direct contact with copper wire, oxidation of the polyethylene is accelerated due to catalytic action of the copper. It is therefore desirable in underwater applications to use a tin-plated conductor in contact with polyethylene and to use crosslinked polyethylene, if possible, containing an antioxidant and with minimum internal stresses.

Lawton [19] reported on the recovery in 1958 of a nonarmored deep-sea submarine telegraph cable that had been layed in 1951 in 7500 feet of water near Nova Scotia. The polyethylene insulation, which deliberately had been left exposed, showed no evidence of attack except for light scorings 1/32 inch deep or less. These were observed only in areas where hemp spun-yarn had been applied. Apart from this damage the cable after 7 years submersion could not be distinguished from its condition when manufactured. Munitz [20] reported on the recovery

of 299 samples of failed submarine telegraph cables in which none of the polyethylene insulation examined showed any signs of degradation.

Muraoka [7,8] reported hardness and water absorption measurements for a large number of plastics that had been exposed up to 2 years. Cellulose acetate, nylon, and poly(methyl methacrylate) showed decreases in durometer readings after exposure. The first two materials also had over 1% water absorption, which would be predicted from laboratory tests.

Lee [13-16] reported the results of mechanical tests on 1/8-inch cast and 1/4-inch biaxially stretched poly(methyl methacrylate) sheet after four ocean exposures in the Pacific at 2300 and 5600 feet for up to 2 years. There was no evidence of biological attack on any of the specimens. The mechanical test results were somewhat erratic. There did not appear to be any appreciable change in tensile strength, flexural strength, or modulus, but there was an indication of decrease in compressive strength.

Wallace and Colletti [12] conducted mechanical and optical tests on six types of polycarbonate sheet after 1 year of exposure at 4200 feet in the Tongue of the Ocean, Bahamas. They found no appreciable change in tensile, impact, or optical properties and no evidence of biological attack.

### Plastic Tapes and Films

Connolly [1] reported that three types of plastic tape (polyethylene terephthalate, oriented polystyrene, and polytetrafluoroethylene) had suffered severe mechanical damage in 7 years. This was caused by fouling organisms growing under overlaps and tearing the tape. Polymono-chlorotrifluoroethylene tape failed after 10 years in the same manner [2]. Muraoka [3-9] reported that a black pressure-sensitive electrical plastic tape 0.010 inch thick was attacked by borers in two out of seven exposures, but the damage consisted only of shallow holes without complete penetration. A gray rubber tape exhibited slight surface cracking but did not fail.

Muraoka [10] exposed poly(vinylidene chloride) (PVDC) and polytetrafluoroethylene (PTFE) plastic films which had been applied to the surface of painted and unpainted carbon steel panels and unpainted stainless steel and K-Monel panels using a pressure sensitive adhesive. These panels were submerged in 20 feet of water near Port Hueneme, California, to determine if the plastic film coverings could be used to protect metal surfaces from fouling and corrosion, to permit removal of marine growth by stripping off the plastic covering, and to prolong fouling-free and corrosion-free intervals. The PVDC- and PTFE-covered panels were exposed for 5 and 8-1/2 months respectively. When retrieved, the panels were completely covered with marine growth. However, the plastic films were in good condition. The PTFE film could be stripped off with little difficulty, removing the marine growth and leaving a clean surface. In the case of the PVDC film, there was heavy crevice corrosion along the edges of the stainless steel panels due to seawater coming in contact with the metal through small rupture holes in the film.

Muraoka also exposed specimens of polyethylene film [5] and poly(vinylidene chloride) film [5,9] for up to 3 years with no evidence of biological attack.

### Plastic Fibers and Ropes

Connolly [1] reported that after 7 years of exposure noncellulosic synthetic fibers gave no indication of either borer or microbiological attack. These included polyacrylonitrile, poly-(acrylonitrile-vinyl chloride) copolymer, polyethylene terephthalate (polyester), nylon, and poly(vinyl-chloride-acetate) copolymer. On the other hand, cellulose acetate and cellulose triacetate fibers were destroyed by borers and microorganisms in 1 to 4 years.

Muraoka [3-9] reported that in seven exposures of up to 3 years, 1/4-inch nylon and 5/16-inch polypropylene ropes were not attacked by borers or by microorganisms. On the other hand, 1/2-inch cotton and manila ropes exposed at the same time were severely damaged by microorganisms and by borers and microorganisms respectively. Strength tests were

conducted on the rope specimens after five of the exposures [4,6-9]. Although the results varied somewhat, in general the nylon and polypropylene ropes retained approximately 80% and 100% of their respective initial strength after exposures of up to 2 years. The cotton and manila ropes, on the other hand, retained 0 to 50% of their initial strength under the same conditions. In one 6-month exposure [9] polyethylene rope retained its full initial strength.

One type of "deterioration" encountered by plastic ropes and insulation is what has been reported as fishbite, occurring at certain depths in some locations and resulting in complete parting of a line in many cases. Stimson [21] reported on the failures of 18 buoy stations in deep water off the coast of Bermuda, in which the 9/16-inch polypropylene mooring cables broke. There was a high mortality rate in the first few days. After the fifth day, the rate dropped and remained remarkably constant through 200 days. Failure was attributed to fishbite, resulting in parting of the line. Stimson reasoned that if the attacks were provoked by the attachment of fouling organisms to the cable, the incidence could be expected to increase with time, but this did not seem to be the case. Turner and Prindle [22] reported on the distribution of fishbites in the lines of two deep moorings that were set in 2000 meters of water off of Bermuda. In one mooring exposed for 1 week in the spring using 9/16-inch polypropylene with a poly(vinyl chloride) sheath, fishbites were found from 400 to 800 meters. The second mooring was exposed for 6 weeks in the fall using 0.145-inch steel cable with a 0.0875-inch-thick polyethylene coating, and in this case fishbites were found from 150 to 1500 meters with diminished frequency deeper than 1000 meters. Turner and Prindle [23] reported further figures on the incidence of fishbite in the polyethylene-coated steel line after exposure of up to 82 days. Most bites occurred between 600 and 1200 meters, with the peak of activity between 900 and 1000 meters. The deepest bite detected was at 1550 meters. From the tooth fragments found and the geometry of the bites, the damage was attributed to a fish *Sudis hyalina*. It is suspected that the fish are attracted by luminescent organisms entangled on the lines.

Muraoka [24] also reported that certain varieties of marine fish are attracted to white polyethylene-covered cables and lines. He recommends the use of black polyethylene-covered cables, since they do not attract fish. Macander [25] reported on the recovery of a deep sea array that had been submerged for 1 year at 4200 feet at the Tongue of the Ocean, Bahamas. There was no damage of any type to a black polypropylene-coated steel wire rope which rested on the ocean bottom or to a black polypropylene rope catenary whose maximum and minimum operational depths were 4200 feet and 2600 feet respectively.

## Rubber and Elastomers

Many rubber materials have been exposed because of great interest in their use as electrical insulation as well as gaskets and seals. These include the materials listed in Table 2.

Table 2  
Reported Exposure Tests of Rubber Materials

Material	References
Butyl rubber	1-9, 14
Chlorinated polyethylene	11
Chlorobutyl rubber	14
Ethylene-propylene rubber	2, 11, 26, 27
Chlorosulfonated polyethylene	11
Fluoroelastomer	26, 27
Natural rubber	1-9
Neoprene	1-9, 12, 27
Nitrile-butadiene rubber	1, 2
Silicone rubber	1-9, 12
Styrene-butadiene rubber	1-9
Polyurethane	2
Vinyl-Buna N rubber	27

The results have indicated, in general, little deterioration in physical properties and good resistance to borers and microorganisms, although there are exceptions. Muraoka [3-9] reported no attack by marine organisms for exposures of up to 3 years for butyl, natural, and neoprene rubbers. Styrene-butadiene rubber exhibited slight damage in two out of seven exposures, but silicone rubber underwent serious surface deterioration in every exposure apparently due to the nibbling of marine animals. Connolly [1] and Connolly et al. [2] reported severe surface cracking of silicone rubber in addition to borer damage. They also reported surface cracking of natural rubber after 6 years, significant borer attack on two formulations of neoprene but not on a third, borer attack on one formulation of styrene-butadiene rubber and surface cracking on another after 7 years, and severe borer attack as well as chemical deterioration in 2 years for an ester-based polyurethane, but they reported no deterioration or attack for an ether-based polyurethane in 5 years. Three formulations of ethylene-propylene rubber showed no deterioration in 5 years, but a fourth exhibited surface blistering in 7 years in areas where fouling organisms were attached. A nitrile-butadiene rubber exhibited no deterioration in 15 years.

Bultman and Southwell [11] exposed chlorosulfonated polyethylene, ethylene-propylene rubber, and chlorinated polyethylene for 8 months to 14 months in the Pacific Ocean at Naos Island, Canal Zone. These materials were attacked by borers on faces in contact with wood but not directly from the water. The intensity of attack was less than that for a series of poly(vinyl chloride) plastics previously referred to and having approximately the same hardness range. It was postulated that this may have been due to a physical peculiarity involving a combination of toughness and elasticity.

Measurement of tensile properties by Connolly after exposure gave the approximate results listed in Table 3.

Table 3  
Approximate Changes in Tensile Properties  
of Rubber Materials After Exposure [1,2]

Rubber	Loss in Strength* (%)	Loss in Elongation* (%)
14 Years of Exposure		
Neoprene	15	35
Natural rubber	20	15
Nitrile-butadiene rubber	40	35
Styrene-butadiene rubber	30	35
Silicone rubber	70	70
4 Years of Exposure		
Polyurethane (ester)	40	25
Polyurethane (ether)	0	50
Ethylene-propylene rubber	0 to 30	25

\*Approximate values.

Colacicco [26] exposed ethylene-propylene terpolymer and fluoroelastomer O-rings for 6 months at 2300 feet. In a second exposure Colacicco [27] exposed ethylene-propylene rubber, fluoroelastomers, vinyl-modified Buna N rubber, and neoprene O-rings for 2 years at 5600 feet. In both cases some of the specimens were exposed while under compression and some while elongated. Numerous properties were determined after the exposures were concluded, including hardness, compression set, permanent set, tensile strength, and elongation. In most cases there was little difference between the exposed specimens and laboratory-aged specimens. In general the tensile strength was not appreciably affected, whereas the elongation decreased 20% to 40% for the materials studied.

Wallace and Colletti [12] conducted various mechanical tests, including tensile, tear, and hardness tests, on various compositions of chlorobutyl and butyl rubbers which had been submerged for 1 year at 4200 feet in the Tongue of the Ocean, Bahamas. In general there was no appreciable change in properties of these materials and no evidence of biological attack. In addition neoprene O-ring seals performed satisfactorily after the 1-year exposure; the mechanical properties of several silicone elastomer products did not change appreciably, but two silicones did degrade.

Muraoka [3-8] exposed 15-inch lengths of electric wire consisting of various types of polymeric electrical insulation, 0.015 inch thick, over No. 16 tin-coated copper wire. Insulation resistance and voltage breakdown at 1000 volts for 10 seconds were measured before and after exposure. In most cases specimens were exposed 0.5 foot above the sediment or 3 feet above the sediment. Some of the specimens of each material were exposed as straight wire (unstressed) and some coiled (stressed). The insulating materials used were polyethylene, poly(vinyl chloride), silicone rubber, styrene-butadiene rubber, and neoprene.

The results were quite erratic. There was no consistent difference in behavior between the specimens exposed 0.5 foot and 3 feet above the sediment or between the straight and coiled specimens. All of the materials in most cases exhibited significant decreases, usually 50% or more, in insulation resistance. However, in spite of these major decreases in insulation resistance, the silicone rubber specimens were the only ones that failed the voltage breakdown test for several of the exposures. These failures were probably due to the surface deterioration of silicone rubber referred to earlier.

## COMPOSITES

Organic-matrix fiber-reinforced composites are of great interest for use in the marine environment because of their high strength, relatively low density, good electrical properties, and corrosion resistance. In evaluating these materials for subsurface ocean use, there are two main areas of concern: biological attack and degradation in properties due to water. A number of ocean exposures have been conducted to determine these effects. The materials exposed included those listed in Table 4.

Table 4  
Reported Exposure Tests of Composites

Material	References
Epoxy/glass laminates	1-4, 6, 8, 13-16, 28
Melamine/glass laminates	3, 4, 6-8
Phenolic/cotton laminates	3-9
Phenolic/glass laminates	13-15
Phenolic/nylon laminates	3, 4, 6, 8
Phenolic/paper laminates	3, 4, 6-8
Polyester/glass laminates	1, 2, 13-16, 28, 29

With only two exceptions none of the materials exposed were damaged by borers. One exception was a phenolic laminate with unidentified reinforcement exposed by Muraoka [7,8]. Marine borers made holes in this material during two exposures in an area where wood was in contact with the plastic. The borers had attacked the wood first and then continued into the plastic. Borers also attacked 3/4-inch-diameter phenolic/cotton laminate rod under the wood bait during two exposures [5,7] and directly from the seawater environment without the aid of any wood bait piece during a third exposure [8] making holes about 1/16 inch in diameter by 1/16 inch deep.

Connolly et al. [2] reported that two epoxy/glass-cloth laminates showed no significant visible change after 9 years of exposure. A polyester/glass-mat laminate exhibited minute pitting after 3 years of exposure, possibly due to microbial damage. There was also noticeable erosion of the resin around the surface fibers. After 8 years of exposure the epoxy

laminates showed an 18% decrease in flexural strength and the polyester laminate showed a 25% decrease, and a roughly linear downward trend in strength appeared to be continuing. The insulation resistance of both types of materials decreased an order of magnitude after 1 year of exposure.

Fried [28] reported on the exposure of glass-reinforced plastic laminates at depths of 5700 feet in the Tongue of the Ocean for 3 years. One was a polyester/Style-1000-Volan-glass-cloth laminate; the other was an epoxy/parallel-filament composite, otherwise unidentified. The polyester laminate was essentially unaffected by the exposure. However the epoxy laminate decreased approximately 15% in compressive strength in 100 days and 50% in 3 years. The interlaminar shear strength decreased approximately 30% in 100 days and 70% in 3 years. Fried pointed out that this behavior was not typical of epoxy/fiberglass laminates and may have been due to the lack of a suitable finish on the glass.

Goldfarb [29] reported the results of exposure tests conducted on polyester/fiberglass laminates immersed in the ocean at Kure Beach, North Carolina, 3 feet below the surface. Groups of specimens were removed each year for 5 years, the fouling scrapped off, and the materials kept under water until tested. No mention was made of biological attack having taken place. There were five types of glass reinforcement, consisting of Garan-finished 181 glass cloth, Volan-finished 1000 glass cloth, 1-1/2-ounce Garan-finished glass mat, Garan-finished woven roving, and a combination of 1000-114 glass cloth with 1-1/2-ounce glass mat.

The best material was the laminate made with Garan-finished 181 glass cloth. This material exhibited a slight increase in flexural properties and hardness and approximately a 20% decrease in compressive strength and Izod impact strength, compared with the original values. The other materials exposed decreased in physical properties by up to approximately 40%, and the largest decreases were usually in compressive properties.

These tests demonstrated what has also been shown in laboratory, namely that the surface finish on the glass reinforcement and the construction and type of reinforcement can have an appreciable effect on the strength retention of laminates. It is also significant that these polyester/glass laminates made in 1954 could be exposed in the ocean for 5 years with a minimal loss in strength. Considerable improvements in resins and in finishes since that time should result in greatly improved performance for current laminates.

Fried and Graner [30] reported on the strength of a polyester/fiberglass composite used for a submarine fairwater. This component was subjected to subsurface and above-surface ocean environment. The laminate was fabricated in 1953 with Style-181 Volan-finished glass cloth and a polyester resin. The fairwater was removed after 11 years of service, and the properties of the material were determined. The flexural strength, measured with the material wet, had decreased approximately 15%, and the flexural modulus had decreased approximately 5%. The Barcol hardness had decreased by only 3 units. The mechanical properties still exceeded the original requirements in the specification.

Lee [13-16] conducted tests on polyester/glass, epoxy/glass, and phenolic/glass laminates that had been exposed for 6 months and 1 year at 2300 feet, 2 years at 5640 feet, and 1 year at 35 feet. The exact composition of these materials was not presented. The results obtained were somewhat variable. The reductions in flexural strength, flexural modulus, and tensile strength varied up to 20%, and the reductions in compressive strength varied up to 40%.

## SUMMARY AND CONCLUSIONS

In evaluating materials for extended use in the ocean, it is necessary to consider the susceptibility to biological attack and to chemical deterioration in water. To assess these factors, many polymeric materials and organic composites have been exposed in the ocean for up to 15 years. Many plastic materials were included, in the form of sheets, rods, films, and ropes. With the general exception of cellulose, these materials were not attacked by marine microorganisms. However, every material can be attacked by borers. When attack does occur, it usually consists of relatively shallow surface scoring. Attack can be precipitated by the proximity of other materials which are highly susceptible to borer attack, such as wood. There is

a greater probability of attack in areas of high marine biological activity — in warm shallow water rather than in colder deep water, and at the ocean bottom rather than away from the bottom. There is some indication that materials with hard surfaces or with smooth, waxy surfaces are not as susceptible to borer attack, but exceptions to this general rule have been observed.

Plastic tapes, which were wrapped around rods for exposure tests, were damaged by fouling organisms attaching themselves and growing under overlaps and tearing the tapes.

Cellulosic fibers and ropes were attacked by borers and microorganisms and were severely damaged, whereas synthetic materials were generally not affected. Nylon and polypropylene ropes retained 80% and 100% of their respective original strength during two years of exposure, whereas cotton and manila ropes retained only 0 to 50%.

Another type of deterioration encountered was that of failure of polyethylene ropes due to fishbite. This has occurred near Bermuda in depths up to 1500 meters and was attributed to the *Sudis hyalina*. It has also been reported that the same effect was not observed for black polyethylene ropes.

Many types of rubber have been exposed, with generally good resistance to borers and to microorganisms and moderate loss in physical properties. Most rubber materials were either not attacked or suffered slight surface damage. The main exceptions were silicone rubber and polyurethane. Silicone rubber suffered severe surface deterioration, probably from marine animals, as well as borer attack. Ester-based polyurethanes are generally not stable in water over extended periods, but the ether-based polyurethanes are. Most of the rubbers exhibited significant decreases in elongation as a result of extended exposure in the ocean.

Several types of polymeric insulation over copper wire exhibited significant decreases in insulation resistance as a result of long-term immersion in water, but only the silicone rubber failed due to voltage breakdown.

The organic-matrix fiber-reinforced composites subjected to extended ocean exposures were not usually attacked by borers or other marine life, but did undergo some degradation in strength properties. The extent of deterioration depends on a number of variables that have been evaluated in numerous laboratory investigations. They include the resin, reinforcement, curing agent, reinforcement surface finish, reinforcement construction, curing conditions, resin content, and void content. The results published indicate that well-fabricated composites will decrease 20% and less in physical properties as a result of several years of exposure in the ocean. Static loading or fatigue loading of the composite during this period will increase the extent of degradation.

As a brief summarization, most polymeric materials will not degrade seriously as a result of extended immersion in the ocean. These materials, with some exceptions, are not attacked by marine microorganisms. Any polymer can be attacked by borers, usually with only slight surface damage. On the other hand the material can be submerged for years with no attack. Now that these general principles of biological behavior have been established, additional extended underwater tests must be viewed as having limited value for polymeric materials. The effect of water on these materials can be determined more exactly and much less expensively in laboratory tests.

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# CERAMICS, PAPER, FABRICS, PHOTOGRAPHIC MATERIALS, AND MAGNETIC TAPE

L. A. Beaubien  
Ocean Materials Criteria Branch  
Ocean Technology Division, NRL

## INTRODUCTION

This section deals with the effect of the subsurface ocean environment on some miscellaneous materials and components having varying degrees of utility for ocean technology applications. The materials included are ceramics, paper, and textiles, and the components covered are photographic materials and magnetic tape. The environmental aspects considered for most of these items are the material deterioration due to the chemical effect of the seawater and biological attack by marine organisms.

Since little or no information was found on these materials from the literature searches, the bulk of this report is based on the experience or opinion of recognized authorities. Not only have there been essentially no organized investigations of the effect of the sea environment on these items, but there is no indication of any such studies being planned for the immediate future.

## CERAMICS

For purposes of this study a ceramic is considered to be any inorganic nonmetal which is formed by either a temperature or a temperature-and-pressure process. This definition includes glass, graphite, alumina (such as substrates for microelectronics), and the commonly recognized ceramics such as the porcelains used for electrical insulation but excludes concretes and cements.

It is the consensus of all ceramists contacted that ceramic materials likely to be used for undersea applications will not be adversely affected by seawater over any reasonable time frame.

With the exception of some data on microscope slide glass drawn from evaluation tests of deep ocean materials conducted by the Naval Civil Engineering Laboratory, no evidence was found of any scientific studies of the effect of seawater on ceramics. However, there are numerous examples from underwater archaeological sites in the Mediterranean, and off the coast of Florida, of ceramics ranging from porcelain to ordinary earthenware which have been unaffected by centuries of immersion. Likewise, although some deterioration of glass has been noted in samples which have been immersed for as long as 200 or 300 years, immersion times of 50 years or less appear to have no deleterious effect. This conclusion is in agreement with results of the aforementioned NCEL exposures conducted in the Pacific Ocean at depths of 2300 and 5600 feet, which produced no noticeable deterioration for exposures up to 2 years [1-5]. The general opinion of ceramists is that most modern ceramics and glasses will likewise not deteriorate over the relatively short times (up to several years) they would be expected to perform in submerged systems.

It should be recognized, however, that some modern ceramics developed specifically for their electrical or optical properties, such as the new chalcogenide glasses used for their excellent infrared transmission, may degrade to some extent in seawater. Specific studies of these materials will be required to determine their sensitivity to seawater.

## PAPER AND PRINTED DOCUMENTS

Since no examples of actual long-term exposure tests were uncovered, the following information on the deterioration of paper and printed documents in seawater is based primarily on discussions with sources experienced in paper chemistry, in particular personnel of the National Bureau of Standards, Bureau of Engraving and Printing, and Institute of Paper Chemistry.

The following general conclusions hold for grades of paper normally used for writing and printing but may not apply to extreme examples such as newsprint and paper specially treated for wet strength:

- The effect of seawater on paper, whether based on cotton or wood fiber, will be no different than that of ordinary fresh water.
- Paper will not disintegrate in water without accompanying mechanical action or biological attack (borers, etc.).
- The tear strength of the paper when wet will usually be considerably less than when dry, but most of the strength will return upon drying.
- The inks used for printed documents will normally last indefinitely in water.

### Paper in General

Paper, whether based on wood pulp or cotton fiber (rag bond, etc.), is a cellulosic material which relies for its strength on fiber-to-fiber hydrogen bonding. When immersed in water these hydrogen bonds are weakened, so that the tear strength of unmodified paper usually diminishes in minutes or hours to a small fraction of the dry strength, with no further change in strength with time after this initial weakening. However, most of the initial strength can be recovered by drying without excessive mechanical action. The addition of sea salts to the water would be expected to have little effect, since seawater is usually slightly basic and paper (cellulose) is generally attacked by acids but not by bases.

Further deterioration, to the point of annihilation or disintegration, would require either biological or mechanical action. The amount of mechanical action required to cause disintegration would depend on the wet tear-strength of the paper, which will vary with the type of fiber and binder. Biological deterioration of paper (actually the cellulose), whether by borers or by microorganisms, is primarily a function of location. Ordinarily paper would not be expected to survive in offshore areas less than 600 feet deep or at any depth within a few feet of the bottom, since these are prime zones of biological activity. However, paper and other cellulosic materials have remained free from attacks when silted over on the ocean bottom for more than 200 years. (see below)

A possible complication in the recovery and preservation of submerged paper is that for tightly packed sheets under pressure the return of hydrogen bonding during drying might also result in the sticking together of adjacent sheets, so that in some cases it might be best to separate the sheets when still wet or at some stage prior to complete drying.

The deterioration characteristics of paper can be modified by wet-strength additives, which are not normally found in writing and printing paper but may be encountered in photographic paper, maps, etc. As an example, a good rag stock combined with a resin modifier can maintain a wet tear strength very close to the dry strength for an extended time. Within this time frame the paper can withstand significant amounts of mechanical action without disintegration. At the other extreme, there are weak papers, such as newsprint, which may deteriorate quickly in water with little or no attendant mechanical action. As with wet-strength paper, these weak paper stocks are not ordinarily used for writing or (except for newsprint) for printing.

## Inks

Printing inks, with the possible exception of newspaper inks, usually consist of a carbon-black pigment combined with a natural oil vehicle. As a result, print using this type of ink has some inherent film integrity and is generally not soluble in water. The likeliest means of disintegration of print is by deterioration of the paper substrate. An ink not labeled washable or water soluble will ordinarily not be affected by water.

## Structural Paper Products

The behavior of paper products such as packing and shipping containers, although similar to that of paper alone, is complicated by the presence of water-soluble adhesives. Containers intended specifically for marine applications use layers of wet-strength paper (combined with waterproofing treatments of the outside surface) bonded together with relatively water resistant adhesive. Containers of this type can be expected to maintain their integrity in water for extended periods of time, but they will eventually weaken, since even the best adhesives presently used are water soluble to some extent. Containers, such as ordinary corrugated boxes, which are not specially designed for marine use would most likely lose their integrity and structural utility in less than an hour, primarily due to dissolution of the adhesive and resulting delamination.

## Example of Silted-Over Paper

In June 1964 an archaeological team working the site of a Spanish galleon wrecked between 1650 and 1700 4 miles off the coast of Florida in 40 to 45 feet of water recovered several pieces of paper which had been silted over on the bottom. When dried, these linen fiber sheets, which were covered with clearly legible gothic print consisting of lampblack and vegetable oil, displayed a strength close to that of the estimated original strength. Although the animal sizing used in making this paper and type of ink used would probably produce a permanence above that of present-day papers and documents, still its survival for such a long time when protected from biological and mechanical action by only a layer of silt would indicate that paper in general can survive in seawater for extended periods of time when properly protected, even in biologically active areas.

## FABRICS (TEXTILES) AND FIBERS

Fabrics can be separated into two categories, depending on whether the fibers used are natural or man-made. The man-made category can in turn be separated into natural-polymer and synthetic-polymer fibers. The behavior of man-made fibers (and therefore of the resulting fabrics) and also the behavior of some natural fibers used for such applications as mooring and towing lines, were covered in the first section, on polymeric materials. Specific discussion in this present subsection is limited primarily to aspects of deterioration of natural fibers which are not covered in the first section.

Natural and man-made fibers are chemically inert in seawater. However, both natural and natural-polymer fibers are usually destroyed by biological activity in 1 to 6 months, although some natural polymers may not be destroyed for as long as 4 years under ideal conditions. Synthetic polymers appear to be generally free from biological deterioration. Since fiber deterioration is strictly biological, it depends strongly on geographical location, depth, and periodic variations in local biological environment.

Natural fibers are either cellulosic (such as cotton, linen, hemp, jute, sisal, kapok, ramie and manila) or proteinic (such as wool and silk) and are chemically inert in pure water but are susceptible to damage by a wide spectrum of biological life. Because of this susceptibility to biological attack, coupled with the relative indestructibility of synthetic polymer fibers and the limited marine utility of fibers and fabrics in general, little information has been published on the deterioration of natural fibers in seawater.

Two sources are a 1921 paper by Dorée [6], and a series of early (1920's) publications by the Bureau of Fisheries [7]. The paper by Dorée is based on controlled laboratory immersion tests on cotton coupled with data from uncontrolled immersion tests at Brighton, England, on a variety of cellulosic and proteinic fibers. The basic results of this study were that untreated natural fibers were completely destroyed by microbiological life in a month or less (except for wool, which lasted a little longer), and that, at least in the case of cellulosic materials, deterioration was solely due to the microorganisms (in the presence of oxygen), with no effect of oxygen or sea salts by themselves. The data from the Bureau of Fisheries, obtained from several geographic sites with differing environmental conditions, supported these findings, with the addition of the conclusions that deterioration might be expected to be greater in summer than in winter, due to a stirring of the bottom during winter, and that there are locations, such as near lime deposits, where biological deterioration can be greatly slowed if not eliminated. The results of both sources on the effect of preservative treatments are too old to be of specific importance; they do indicate that such treatments can prolong the useful life of natural fibers for several months but not indefinitely.

An additional characteristic of natural fibers is that cellulosic fibers increase in strength when wet. For example the wet strength of cotton increases up to 25% [8].

The Textile Technology, Charlottesville, Virginia, provides a comprehensive abstracting service covering all journals, both foreign and domestic, concerned with the production and performance of fabrics and fibers. It is unlikely that descriptions of any recent or future work by the textile community on the deterioration of either natural or man-made fibers would not be found in this digest.

## PHOTOGRAPHIC MATERIALS

Inquiries were made to various manufacturers and processors of film, as well as to government and private organizations which would be likely to encounter the problem of recovery or processing of seawater-contaminated film. The meager information that was uncovered is based on limited, and often undocumented, tests by the sources mentioned, as well as on the opinion of personnel with considerable experience in photographic chemistry. Since the information uncovered dealt almost exclusively with exposed but undeveloped film, this case will be assumed in the following discussion unless otherwise stated. Likewise, only black-and-white film is considered, since no information could be found on color film.

There seemed to be some difference of opinion among the sources, but some generally accepted conclusions are the following. Exposed but undeveloped film at room temperature will lose some image density over the first day or two of immersion in seawater which may or may not be 100% recoverable depending on the type of film used. This deterioration of the image is less at a lower temperature, so that images on some films may be essentially unaffected after exposures of as long as a month at 0°C. Generalized interpolation between these extremes of time and temperature on the basis of existing information is not possible. Also since image degradation is a chemical process, the environment can be important, such as whether the film is close to metal surfaces. In all cases experimentation is required with part of the film to determine the developing procedure for the remainder.

## Chemical Effects

Experience at E. I. duPont de Nemours and Co. with photorecording tape, described as similar to camera film, coupled with some tests, indicated that undeveloped film will undergo rapid loss of image (80% loss) after 3 to 4 hours exposure in water due to chlorine fogging. However, a fresh-water washing can eliminate most of this fogging and allow recovery of almost all of the image. Limited tests at NRL [9] on Plus X film submerged in synthetic seawater at room temperature indicated a serious degradation of the image after 1 day and complete destruction of the image after 4 days. However, the same test procedure at 0°C showed essentially no loss of image after 4 days of immersion and a gradual loss thereafter through

the 35-day duration of the test, at which time usable images were still recoverable. These NRL tests involved a standard development procedure which was not experimentally varied as a function of immersion time.

According to the same duPont source, an immersion of weeks or longer is accompanied by a more permanent type of fogging, due to the action of organic sulfur and similar compounds, which produces an overall blackening of the image. It was then predicted that some information could still be salvaged by experimenting with restrainers during processing. It was also expected that this fogging would increase with depth, although this increase with depth would tend to be offset by the protective influence of lower temperatures. These opinions would appear to conflict somewhat with the results of the limited NRL tests, again using standard rather than experimental development techniques, which indicate a complete loss of image after 4 days of immersion except at very low temperatures.

The single example uncovered of retrieval and processing of saltwater-contaminated film is that of a rocket spectroscopy package recovered from 6000 feet of water after 14 days of immersion. Usable images were obtained from one camera having Teflon-coated internal surfaces, but none were obtained from the other uncoated cameras. The exotic nature of this particular nongelatinous film precludes immediate application of these results to more conventional films. However, it does point out the possible sensitivity of photodeterioration in seawater to chemical reaction with the surrounding media.

#### Nonchemical Effects

The effects mentioned have been purely chemical and applicable only to undeveloped film. No information appears available on either processed negatives or prints, but the opinion of most sources is that deterioration of these items would be primarily nonchemical. Most film and prints have a gelatinous emulsion which is soluble in water. In the case of developed and undeveloped film, the backing is relatively indestructible in seawater, so that any deterioration would have to consist of either a loosening of the bonds in the gelatin to such an extent that it could float away from the backing (an untested possibility which is a point of apparent disagreement among the sources) or of some attendant mechanical action which would scrape the softened gelatin from its backing. In the case of rolled film the expanding gelatin might either ooze out the sides of the roll or mechanically damage the plastic backing, causing distortion or destruction of the image. A further problem for rolled film, and also for closely packet sheet film, would be sticking of the expanded gelatin to the uncoated face of the neighboring film, with attendant problems of separation. Hence films and prints should be kept immersed in water after recovery while awaiting processing.

In the case of prints the softening of the gelatin is accompanied by a weakening of the hydrogen bonds in the paper, producing a sensitivity to lesser mechanical actions that might not scrape off the gelatin but which could cause disintegration of the backing and therefore of the print. Limited tests at NRL in completely quiescent water indicate that photographic paper is not likely to disintegrate when immersed in water for considerable times (weeks or longer) without mechanical agitation. However, these same tests did produce one example of complete disintegration and separation of the gelatin coating from its paper backing after 4 to 6 weeks of immersion, without any noticeable effect on the paper backing. Unfortunately this example infers nothing about the possible disintegration of gelatin on a film backing because of the different nature of bonding.

#### Handling Procedure

The following procedure, essentially that proposed by Eastman for handling film that has been immersed in seawater, appears to be the consensus, based on the assumption of the most extreme case: a tightly rolled undeveloped film.

If there is any sticking of the layers due to the softened gelatin, either at the edges or throughout the roll, then the best separation technique must be determined by experimentation. The following steps, which must be carried out in the dark for undeveloped film, are suggested:

Attempt to separate the film immediately after removal from water, without allowing any drying; in severe cases separate the film under water, possibly with the use of a neutral wetting agent and/or a 5% sodium sulfate solution to suppress swelling of the gelatin; immerse in a rehardening bath such as a stop bath of acetic acid and sodium sulfate, or in extreme cases a formulation hardener; if the undeveloped film is exposed, experimentally process it; wash in alkaline wetting agent solution and carefully wipe both base and emulsion surfaces.

For the step of experimentally processing exposed undeveloped film the following is recommended. A sample of the film should be tested first in the recommended developer. This sample preferably should be taken a considerable relative distance into the roll. If fog is apparent, then it is necessary to modify the developer to produce the maximum differentiation between fog and information (image). It is suggested that the entire roll be bathed in a 1.0-gram-per-liter KBr solution prior to development. Then a series of small strips should be tested to determine how much bromide (a restrainer) should be added to the developer and how much development time is required to produce the best result. This concentration may range from 20 to 40 grams per liter of developer, and the time of development may range from seconds to minutes.

## MAGNETIC TAPE

Inquiries were made of tape manufacturers as well as of government organizations which would be likely to encounter the problem of seawater-contaminated magnetic tape. These inquiries uncovered no examples of either accidentally immersed tapes or tests of the effect of seawater on such tapes. However, the consensus was that the effect of seawater on a finished-product tape would differ little from the effect on the individual components: plastic backing and metal-oxide-plus-polymer-binder coating. The type of magnetic tape likely to be used or encountered in marine applications (polyester-backed tape) will ordinarily not deteriorate in seawater. However during extended submersion in biologically active areas marine organisms may grow between the layers and cause mechanical damage.

### Backing

The backing of magnetic tape is a plastic material, usually polyester but sometimes cellulose acetate, and is generally considered to be free from chemical attack by seawater. The only documented type of damage to polyester tapes similar to the backing used for recording tape appears to be a mechanical rupturing reported by Connolly [10] of an insulation tape immersed in seawater for 7 years. This rupturing was caused by the growth of marine organisms which had worked their way in between the tape and the rods on which they were wrapped. Although no information was found on cellulose acetate tapes as such, Connolly reported examples of complete destruction of cellulose acetate fibers within 1 to 5 years by marine organisms. Connolly's studies were in a shallow region of high biological activity.

### Coating

The coating usually consists of a proprietary mixture of many constituents (possibly 20 or more) but for purposes of behavior in seawater can probably be considered as a mixture of magnetic oxide particles in a polymer binder. This mixture in its solidified form should be chemically inert in water. The oxide particles, which may be iron, chromium, etc., should also be free from deterioration, since they are already oxidized and as such are not susceptible to further oxidation.

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## ELECTRONIC COMPONENTS

C. L. Buchanan  
Ocean Instrumentation Branch  
Ocean Technology Division, NRL

### INTRODUCTION

Many experiments have been conducted to determine the effect of hydrostatic pressure on electronic components. The results of these tests indicate that most requirements for electronic circuit components can be met by proper selection of off-the-shelf components. The only type of circuit element which could not be operated under pressure was the general family of mechanical resonators such as tuning forks and crystals. A literature search revealed, however, that few experiments were conducted (and even fewer reported) in which circuits or circuit elements were subjected to seawater under pressure.

The literature search, on the degradation of electronic equipment caused by its protracted immersion in seawater at some appreciable depth, was conducted via the Defense Documentation Center and via individuals known to have worked in this field. The type of equipment considered of interest was equipment designed for use in conventional environments, not those especially designed for deep submergence. The DDC search yielded almost no useful information. The majority of the applicable literature came from journals, internal reports, and symposium proceedings, not included in the DDC files. The end of this section is a bibliography of work of sufficient interest to warrant inclusion. No experiments were performed expressly for this study, although the investigation of damage to electronic equipments from the submersible Alvin, which were exposed to seawater at a depth of 5100 feet for 9 months, was underway during this study and will be reported here.

### TYPES AND EXTENT OF DAMAGE

An operating electronic device immersed in seawater may incur three serious types of damage: short circuiting due to the seawater, electrolytic action, and collapse of components due to hydrostatic pressure.

#### Short Circuiting

Short circuiting (assuming the existence of normal operating potentials) may overload some of the components and destroy them by excessive currents. If internal batteries are used, these currents may persist for a fairly long time, and the batteries themselves may be overloaded causing heating or even rupture. A rupture may release chemicals which have additional corrosive effects.

The literature contains almost no information on short-circuit damage to operating circuits which were accidentally flooded. In numerous cases in the author's experience, extensive damage was unusual. Usually only one or a few connecting wires or terminals would burn out and the remainder of the circuit would be intact. The damage was normally localized at the point to which the power was supplied to the circuit. With printed circuits the connecting wires are usually much larger than the circuit-board conductors so the circuit-board conducting material is destroyed, although the previous location of this material is normally visible.

## Electrolytic Action

When an operating circuit is immersed in seawater, two types of electrolytic action can be expected. If internal power is supplied to the equipment during immersion, the circuits carrying current will be subjected to severe electrolytic action, and some of the conductors will be removed and deposited in other areas. After the internal power is dissipated, the long-term electrolytic corrosion continues, driven by the dissimilar metallic components in the common seawater electrolyte.

Much information has been developed on electrolytic corrosion in experiments in which metal samples are electrically isolated from each other. The literature is silent however on damage to actual equipment containing combinations of different metals and other materials under these conditions.

The equipment removed from the submersible Alvin is one of the best sources of information. In this case the equipment was not powered at the time of immersion, so no damage due to short circuiting occurred. The damage caused by electrolytic corrosion was obvious. Even the most cursory inspection of the circuit boards permitted easy location of every piece of ferrous metal in the assembly. A surprising number and variety of electronic components use ferrous connecting leads. Several types of capacitors and numerous transistors contained ferrous leads, and these were frequently corroded to the point of being physically detached. The area of the circuit board surrounding these connectors was clearly visible due to the characteristic rust coloring. For similar components in redundant circuits, there was a high degree of uniformity in the corrosion in spite of differences in physical location.

Electrolytic action was most damaging in electromechanical devices where small sizes of copper wire are close to ferrous metals. Motors, meters, and relays were generally damaged beyond further use.

## Hydrostatic Pressure

If an electronic circuit is exposed to appreciable hydrostatic pressure, certain components will deform or collapse. The results may be of no consequence in some cases and may be catastrophic in others.

The literature deals mainly with the hydrostatic effects on the electronic-circuit components. While this literature is mostly concerned with the determination of the characteristics of the components while under pressure, the data usually also consider the characteristics after the pressure has been removed.

The most severe and catastrophic damage occurs in glass envelopes such as oscilloscope tubes and other vacuum tubes. Implosion of cathode-ray tubes in several of the Alvin electronic equipments did essentially no secondary damage. The shields surrounding these tubes were not distorted or scarred as might have been anticipated. This observation holds for other vacuum tubes which were not enclosed in shields, although there were few such tubes in the equipment.

Much of the literature is concerned with semiconductor devices. The conclusion reached is that the semiconducting material itself is not seriously altered by the application of triaxial stress. The actual component however may react very differently due to the particular mechanical design of the protective enclosure.

A standard TO5 transistor case is a good example. The electronic equipment from the Alvin contained hundreds of TO5-style transistors, which were all severely deformed by the 2200 pounds of hydrostatic pressure. The deformation was uniform and consisted of inward collapse of the top of the transistor cover. These caps are usually constructed of steel. In most cases the metal deformed into a new shape strong enough to withstand the pressure. Such units operated as well as before as far as could be determined. In the few instances of failure the metal either deformed far enough to make contact with the semiconductor chip itself or cracked and allowed the unit to flood.

Semiconductors in glass envelopes are usually able to function after being subjected to high pressure. However, in the Alvin electronics, in which hundreds of glass diodes were used, the diodes showed a high failure rate after being put back in service. In some cases the glass envelopes were partly flooded, and when the temperature rose during equipment operation the envelope would burst open. In other cases the glass envelope was broken either at the time the pressure was applied or during its removal. The vibration or thermal stresses caused by operating the equipment would then cause the diode to malfunction.

Resistors appear quite immune to permanent damage by hydrostatic pressure. While the pressure is applied, carbon composition resistors have been observed to decrease in resistance substantially. There has been no indication that a permanent change occurs. Film-type resistors and wire-wound units show little change even while under pressure. The only type of resistor which has been observed to be unreliable after being under pressure was a glass-encapsulated precision unit. These components behaved similar to the glass diodes.

Numerous types of capacitors are employed in electronic circuits. Many of these types were tested during and after application of hydrostatic pressure. In the most general case it is concluded that if the unit does not contain void space, or bubbles of air or gas, the unit will show little change due to the application of pressure. One exception is polarized high-dielectric-constant barium titanate capacitors. Such units may show a change during and after pressurization.

The permanent damage to capacitors is usually associated with deformation of the case of the capacitor. Often the aluminum case of wet-electrolyte capacitors has been severely distorted by application of pressure. Such components may not show a change in capacitance but will usually no longer withstand the full rated voltage. The many types of capacitors molded in plastic usually operate satisfactorily both during and after the application of pressure.

The literature contains numerous examples of operation of inductors under and after pressure. Those which contain iron powders in a plastic matrix will usually show an inductance proportional to pressure. This is not a permanent change however. The only case covered in the literature of a large permanent change was a special grain-oriented core constructed for square-loop operations. No case is treated in which computer-type core materials were tested. Such components would probably be rendered inoperable by a single application of pressure, since they use materials similar to the grain-oriented square-loop core.

The mechanical components such as switches, plugs, sockets, panels, and enclosures are not treated in the literature cited. Experience with the equipment removed from the Alvin indicates that such components show little damage due to long exposure to the sea.

#### POSTSUBMERSION TREATMENT OF EQUIPMENT

Reference has been made to the condition and behavior of the electronic equipment removed from the Alvin after her 9-month submersion at 5100 feet. It is important that the conditions under which this uncontrolled experiment was conducted are understood. The absence of power at the time of submersion, the intact hull, and the careful handling and cleaning after retrieval minimized the damage. The electronic equipment would have been severely damaged after it was removed from the water if it had been allowed to remain in the air without being cleaned.

During the 9 months exposure at 5100 feet the equipment was surrounded by the intact hull. The only access through which water circulation was possible was the open hatch. Undoubtedly this prevented any extensive intrusion of benthic fauna or sediment.

When the Alvin was recovered, special precautions were taken to avoid damage to the equipment due to exposure to the atmosphere. Most of the water was pumped out before the Alvin was lifted from the water onto a floating barge. Immediately thereafter a viewport was removed, allowing most of the remaining water to drain out. The electronic equipment was immediately removed from the submersible and placed in containers filled with fresh water.

The total time during which the equipment was exposed to the atmosphere was only 1 hour or so. At a later time when adequate equipment and trained personnel were assembled, the equipment was treated by standard techniques [1] to remove the salt water.

## SUMMARY AND CONCLUSIONS

The literature review indicates a scarcity of information directly related to deterioration of electronic equipment when exposed to the ocean environment at an appreciable depth. The three main causes of deterioration are considered to be short circuiting of power circuits, electrolytic corrosion, and hydrostatic-induced deformation.

Short circuiting has no literature cited. The experience of the author indicates that damage from short circuiting is highly localized and renders the circuit completely inoperable but does not destroy components more critical than batteries and cables.

Electrolytic corrosion likewise has not been specifically treated in the literature. There is a wealth of information on electrolytic corrosion of individual metallic materials in seawater but not of several metals in intimate contact as commonly occurs in electronic equipment. The author's experience is that the corrosion is highly selective, mostly against ferrous material, and does not destroy the equipment in the sense that it cannot be refurbished or rebuilt. In fact the Alvin equipment did not look like it had been submerged after a thorough cleaning

Hydrostatically caused deformation has been rather extensively discussed in the literature. Hydrostatic pressure will completely destroy void-containing objects such as vacuum tubes or capacitors. Still the damage to the permanent parts of the equipment has been insignificant. Most of the passive circuit components will survive high pressures, and many of the active components likewise will show little change.

In general, although the damage to electronic equipment caused by exposure to the sea will be extensive, it will not preclude refurbishing of the equipment if such is required.

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## ANNOTATED BIBLIOGRAPHY FOR CORROSION OF METALS

L. A. Beaubien  
Ocean Materials Criteria Branch  
Ocean Technology Division, NRL

### INTRODUCTION

Many publications are available on corrosion of metals in seawater. Presented here is an annotated bibliography representing, within the limitations in scope to be described in the next subsection, the major recent work in this field. Special attention should be called to two of the entries. One is a recent book on marine corrosion by Fink and Boyd (entry 70) which contains the most comprehensive collection yet published of facts and data on various types of seawater corrosion, arranged according to both material and environment. The other is an earlier profusely indexed and crossreferenced bibliography compiled by Keene (entry 117) which covers practically all topics related to marine corrosion, including foreign entries, but is not comprehensive on most topics, including the areas covered in this report.

### SCOPE

This bibliography deals primarily with the corrosion of unstressed, unprotected metals immersed in quiescent seawater at ambient temperature. Such topics as biological fouling, stress corrosion cracking, cathodic protection, and corrosion at high temperatures, characteristic of desalination equipment or at high velocities characteristic of turbine operation are not generally represented. Exceptions are citations for individuals or groups working on a wide range of marine corrosion problems, documentation of their work being more or less complete. Also, when no abstract was available and selection was based on title alone, some latitude was taken on title evaluation.

The resulting entries date primarily from the last 10 to 15 years, with some few entries going back to the middle 1940's. No attempt was made to uncover items which predate presently available abstracting and indexing services. Entries are primarily limited to publications in English except for a few title translations. Further foreign-language entries can be found in the aforementioned work of Keene. The abstracts presented are either those of the original author or are from some outside bibliographic source. However, some editing was done on the longer abstracts from the Prevention of Deterioration Center.

### AVAILABILITY OF ENTRIES

Some of the reports on U.S. Government sponsored work, namely some items with AD numbers, have distribution limitations which can be ascertained by contacting the issuing agency or author. Abstracts of such limited-distribution items have been excluded.

### ARRANGEMENT

References are listed alphabetically and numbered according to the first author named and chronologically under each author. Coauthors' names are given in the original entry but are not considered in the order of arrangement. All authors and coauthors are listed in the author index. An index by material is also given.

**ACKNOWLEDGMENT**

The assistance of Miss Eileen Pickenpaugh and her staff in the Bibliography Section of the NRL Library in arranging and indexing this material is greatly appreciated.

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Ailor, W. H. and Reinhart, F. M.  
CORROSION OF ALUMINUM ALLOYS IN SEA WATER.  
J. Am. Soc. Nav. Engrs., 76: No. 3:  
443-449, 1964.
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- Results of tests, carried out for periods from 6 months to 3 years, on corrosion by sea water of panels of following alloys 1050-H18, 8099-18, 3003-H18, Alclad 2011, and 5050 are given. Same type of corrosion has been studied on galvanized steel sheet.
- 2  
Ailor, W. H. ALUMINUM IN SEAWATER.  
Geo-Marine Technology, 1: No. 4: 38-42, 1965.
- 3  
Ailor, W. H. EVALUATION OF ALUMINUM PANELS EXPOSED IN THE PACIFIC OCEAN AT 2,340 FEET FOR SIX MONTHS. Metallurgia, p.3-12, March 1967.
- Results obtained from the exposure for six months of thirteen alloys at a depth of over 2,300 ft. in the Pacific Ocean substantiate the excellent seawater characteristics of aluminum and its alloys. These results confirm the desirability of using aluminum-magnesium alloys for marine applications and show the effectiveness of cladding in protecting aluminum-zinc-magnesium-copper core alloys. The attack on aluminum alloys in deep-sea exposure generally takes the form of pitting, as in marine surface and atmospheric exposures. This pitting is of a magnitude which is of little consequence for those alloys designed for seawater applications and is comparable to depth of pitting found in surface exposures. No fouling was evident for panels exposed at test depth. A shiny iridescence was observed on some panels. Results indicate that such high-strength alloys as 7079 and X7002 can be used for seawater applications when properly protected by a higher potential cladding alloy such as 7077.
- 4  
Ailor, W. H. EVALUATION OF ALUMINUM AFTER ONE-YEAR DEEP SEA EXPOSURE.  
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Ailor, W. H., Jr. ALUMINUM ALLOYS AFTER FIVE YEARS IN SEAWATER. In: Materials Performance and the Deep-Sea Symposium Papers American Society for Testing and Materials. Seventy-first Annual Meeting, (Held in San Francisco, Calif., June 23-29, 1968) ASTM Special Technical Publication 445. p.115-130, Feb. 1969.
- Eight aluminum alloys and panels of high-purity aluminum were exposed for five years in seawater at Harbor Island, N. C. Replicate 4 by 12-in. panels of each material were exposed in half-tide immersion and full immersion. Removals in triplicate were made at the end of one-, two-, and five-year exposures. Other than the 1199 aluminum (99.99 percent purity), seven aluminum-magnesium alloys (5000 series) and one aluminum-zinc-magnesium-copper alloy 7079 were tested. Panels were degreased prior to exposure and were cleaned ultrasonically in a chromic-phosphoric acid solution after exposure. After depth of pitting was measured, tension specimens were cut from each panel, and the ultimate tensile and yield strengths and elongations were determined. All panels were heavily fouled with barnacles and other marine growth for all exposure periods. The fouling apparently had some effect on the pitting depth of the aluminum in tidal immersion. Little change in tensile properties after five-years' exposure was noted for the 1199, 5083-0, 5086-0 or 5454-H32. Tensile losses were recorded for several alloys as follows: 5086-H112 (4.8%), 5154-H38 (6.2%), and 5457-H34 (4.3%). The high-purity 1199 and alloys 5154-H38, 5086-H112, and 5456-H321 showed losses of 6 to 10 percent in elongation while the change in elongation for the 5457-H34 was a decrease of about 16 percent. The 7079-T6, which can only be used in seawater when protected, had severe exfoliation corrosion. Confirming other work, we found the corrosion rates to be greater for the full-seawater immersion than for the tidal immersion. The lowest five-year corrosion rate in the half-tide location was 0.07 mdd (milligrams per square decimeter per day) for the 5083-0, and the highest rate for the aluminum-magnesium 5000 series was 0.11 mdd for the 5454-H32 alloy. In full-immersion tests the lowest rate was 0.12. For comparison, the rates for the 7079-T6 alloy were 0.79 mdd in tidal and 3.4 mdd in full immersion. Corrosion weight losses and depth of pitting had reduced rates of growth over the interval between two years and five years. Maximum depth of pitting for an alloy was generally at least four times the magnitude of the average of the twenty deepest pits. The deepest pit found for any alloy after five years was 33.0 mils for 5456-H321 in half-tide immersion and 38.0 mils for the same alloy in full immersion. Least pitting depth occurred in 5457-H34 (less than 4.5 mils for both exposures).
- 6  
Alexander, A. L., Forgeson, B. W., Mundt, H. W., Southwell, C. R. and Thompson, L. J.  
CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 1 - FIVE NON-FERROUS METALS. Corrosion, 14: No. 2: 33-41, February 1958.

7

Ambler, H. R. PRELIMINARY REPORT ON CORROSION OF SOME COMMON METALS IN SEA AND CREEK WATER. Gt. Brit. Tropical Testing Establishment, Port Harcourt, Nigeria, Report No. 335: 4 p., March 1954.

Preliminary results are given on the corrosion of sheet samples of sandblasted mild steel, brass, and aluminum immersed in tropical waters at Lagos Harbor (0.22-3.00% salinity, pH 7.2-8.0, temperature 25.5-29 C) and at Port Harcourt Creek (1.3-2.08% salinity, pH 7.2-8.0, temperature 27-29.5 C). In addition, laboratory exposures were made in static and aerated creek water, static and aerated distilled water, and static boiled distilled water.

Corrosion of mild steel was high, up to 70 mil per yr. It corroded most on tidal immersion and less than half as much under total immersion. Brass, however, corroded much more on total than on tidal immersion. Aluminum showed no regular effect. Corrosion in the laboratory with creek water, aerated or static, was much less, particularly for brass, than in the actual creek exposure, suggesting the influence of biological factors. A mild steel panel totally immersed at Port Harcourt for 2 1/2 mo and subsequently placed in dilute acid, produced a strong smell of hydrogen sulfide, suggesting activity by sulfate-reducing bacteria. A similar panel, examined after 2-wk exposure, produced no detectable hydrogen sulfide. Aerated distilled water was as corrosive under laboratory conditions as was creek water for steel, but not for brass.

8

Anderson, D. B. and Vines, R. F. ANODIC CORROSION OF PLATINUM-GROUP METALS IN SEA-WATER. In: Proceedings 2nd Internat. Congress on Metallic Corrosion, New York, 1963, p. 763-766: 1966.

Tests were conducted on Pt, Pt alloys and Pt-group metal alloys, and showed Pt anodes were uniformly consumed at an average rate of 6-7 mg/amp. year in sea-water over a wide range of c.d. Pd, Ag, Pd-40 percent Ag, Pd-10 percent Ru, and Pd-10 percent Rh alloys were consumed at excessive rates; Pt-(5 and 10 percent) Ru, Pt-(5 and 10 percent) Ir, and Pt-(5 and 10 percent) Rh behaved slightly worse than unalloyed Pt, while Pt-12 percent Pd and Pt metal were hardly affected. Test results and apparatus are detailed.

9

Anderson, E. A. ZINC IN MARINE ENVIRONMENTS. Corrosion, 15: No. 8: 409t-412t, 1958.

10

Anonymous. MARINE EXPOSURE TESTS ON Ti-AL AND Zr-AL COUPLES. Light Metals, 16: p. 223, July 1953.

Results of preliminary corrosion tests indicate that full precautions in marine exposure are probably necessary when either titanium or zirconium is used in conjunction with aluminum alloys in any composite assembly involving a joining system.

In these tests three specimens were prepared. (1) Titanium sheet was riveted to A4D aluminum alloy sheet with zinc chromate paste between faying surfaces, (2) zirconium replaced titanium in a similar combination, and (3) Titanium was riveted to A4D sheet without jointing compound. The specimens were tied to stakes in the Menai Straits in such a way that sea water and atmospheric exposure times were about equal. Visual examination after 2 mo showed the titanium and zirconium to be unaffected. The aluminum alloy in both specimens using jointing compound was severely attacked, pitting was particularly severe in areas of distortion produced by stamp marks. The attack on the aluminum alloy was not quite as severe in the specimen joined without chromate.

11

Anonymous. SEA WATER TESTING FACILITY EXPOSES METALS AND ALLOYS TO VARIOUS CORROSIVE ENVIRONMENTS. Materials Protection, 7: No. 10: 58-59, Oct. 1968.

12

Anonymous. THE BEHAVIOUR OF STAINLESS STEEL IN SEA-WATER. Anti-Corrosion Methods and Materials, 14: No. 7: p. 9-11, July 1967.

Presents a critical examination of the behavior of stainless steel in seawater. The behavior varies but alloys containing nickel (austenitic) have the highest corrosion resistance and are the ones most likely to be used. Both pitting and stress-corrosion cracking are discussed. The behavior of stainless steel in chloride solutions, at areas of oxygen shielding and when pitting in the presence of stress, suggest caution and careful use. Many design authorities do not permit the use of stainless steels in any marine environment where the chances of oxygen screening and stress may occur.

13

Anonymous. RESISTANCE OF ALUMINUM ALLOYS TO SEA WATER AND AIR. Rev Aluminium, No. 330: p. 473-478, Apr. 1965.

Corrosion tests on A-G3, A-G4, A-G4MC, A-G5 and A-Sg Al alloys under conditions

simulating those in superstructures of ocean-going vessels. A-G4 grade, currently used in naval construction, withstood all types of tests best. Both bare and painted specimens stood up well in immersion or alternating immersion-emersion tests of several years' duration, while high-corrosion rates were found in semi-immersion tests and in specimens near water-air separation surface. Riveted steel-Al alloy assemblies exposed to sea air behaved well when joint was made with strip of insulating material between metals, or at least with coat of zinc chromate paint. In total immersion tests in sea water on same types of joints, heavy corrosion of Al alloy in contact with insulation strip occurred when Al alloy was not painted or when belts or rivets were not tightened sufficiently or spaced closely enough to provide perfectly tight joint. Even best assembly procedures were not sufficient to guarantee electrical insulation between Al alloy and steel when joints were wet, as in presence of stagnant water, although use of toxic organic-base paints was helpful in these cases.

14

Babakov, A. A., Ulanovskii, I. B., Tufanov, D. G., Korovin, Ye. M. SEA-WATER CORROSION OF STAINLESS STEELS. Akademiya nauk SSSR. Institut fizicheskoy khimii. Trudy, No. 8: Moskva, 345-353, 1960.

In Russian.

An extensive study has been conducted on the corrosion behavior of various stainless steels in Black Sea waters. Five steel groups were tested: 1) steels of the 2X13 (AISI 420) type, plain and with additions of Mo, Cu or B; 2) steels of the X17H2 (AISI 431) type, plain and with additions of Mo, B, or Al; 3) steels 1X18H9T (AISI 321) and 1X18H11B (AISI 347); 4) a series of experimental steels containing 18% Cr and 6-11% Ni with addition of Cu, Nb, Ti, N or B; and 5) a series of experimental Cr-Mn steels containing 13-14% Cr, 13-14 or 18% Mn with additions of Ni, Cu, Ti or N. The most promising results were shown by X17H2 steel additionally alloyed with 2% Mo, by 1X18H11B steel, and by an experimental steel with 18% Cr, 6% Ni, 1.18% Cu, 0.82% Nb and 0.30% N. The respective weight losses after a 2-year test (3 months for X17H2 steel with Mo) were 0.1, 0.36, and 0.39 g/dm<sup>2</sup>. Steel of the 2X13 type were severely damaged during the first three months of the tests. Corrosion was mostly of the localized (in areas of contact with nonmetallic holding devices and barnacles) and pitting type. The weight losses varied between 1.5 g/dm<sup>2</sup> for steel with an addition of 0.96% Cu to 2.8 g/dm<sup>2</sup> for plain 2X13 steel. The X17H2

steel corroded in the same manner, but to a much lesser degree. The weight losses varied from 0.1 g/dm<sup>2</sup> for steel with 2% Mo to 0.9 g/dm<sup>2</sup> for steel with 0.003% boron. Mo in amounts below 2% had no beneficial effect. Of the austenitic Cr-Ni steel the highest weight loss, 1.20 g/dm<sup>2</sup>, was shown by 1X18H9T steel. Also in this case the corrosion was of a localized type. The weight losses of austenitic Cr-Mn steels were high and varied (in the 2 year test) from 5.4 to 6.3 g/dm<sup>2</sup>.

15

Bailey, G.L. COPPER-NICKEL-IRON ALLOYS RESISTANT TO SEAWATER CORROSION. J. Inst. Metals, 79: 243-292, July 1951.

This report describes the development of copper alloys containing 5-10% nickel and 1-2% iron. These materials are easily worked and are resistant to corrosion by moving sea-water.

The corrosion resistance of 70:30 cupronickel to moving aerated sea-water is greatly increased by the presence of 0.30% iron. Iron contents of 1% or more increase the tendency of this alloy to local pitting at areas shielded from oxygen. Alloys of low nickel content (5-10%) are greatly inferior to the 70:30 alloy if the iron content is below 1%; the addition of 1.3-2% iron confers on these low-nickel alloys corrosion resistance of the same order as that of the 70:30 alloy containing 0.3-0.5% iron.

Alloys containing 5-10% nickel and 1-2% iron offer optimum resistance to sea-water corrosion when quenched from temperatures of the order of 850-950 C. The resistance is reduced, particularly in contaminated waters, by annealing at, or slowly cooling to temperatures of the order of 600 C. The reduction in corrosion-resistance accompanying these heat treatments is due to the separation of a second solid solution richer in nickel and iron.

Optimum corrosion-resistance is not compatible with hot workability. Heating to 600-700 C during hot working causes breakdown of the corrosion-resistant structure and increases liability to cracking. The corrosion-resistance of the alloys, as normally manufactured in tube form, is ordinarily not sufficiently below the optimum to justify the troublesome steps necessary to ensure the best possible results. Whatever the heat-treatment or structure, alloys containing 5-10% nickel and 1-2% iron can be readily cold-worked and hot worked if suitable precautions are taken in manufacture.

16

Baker, H. R., Bolster, R. N., Leach, P. B.,

Singleterry, C. R. EXAMINATION OF THE CORROSION AND SALT CONTAMINATION OF STRUCTURAL METAL FROM THE USS TECUMSEH. Naval Research Laboratory. Report No. NRL-MR-1987. AD-687 394. 18 p., Mar. 1969.

The USS Tecumseh, sunk during the Civil War battle of Mobile Bay, is to be raised by the National Armed Forces Museum. Structural specimens were studied to determine the effectiveness of various methods of removing seawater salts from the corroded metal. The nature of the scale deposits and the extent of corrosion were also studied. With the exception of the rivets, the wrought iron of the hull was found to be in surprisingly good condition. The peened ends of the rivets had been deeply attacked, and cast iron deck plates had been perforated in places. Hull joints had been penetrated by corrosion and seawater. Ultrasonic cleaning was found to be ineffective in removing salts due to their encapsulation by the scale. Sandblasting to remove the scale, followed by flushing with water, appears to be the best cleaning technique. Analysis and examinations of the scale showed that there were typically 3 distinct layers, 2 of iron oxides and an exterior calcareous accretion. The formation of the scale layers can be explained by accepted corrosion mechanisms.

17

Basil, J. L. REPORT ON THE RESISTANCE TO CORROSION OF CAST AND WROUGHT ALUMINUM ALLOYS IN SEA WATER; ALUMINUM COMPANY OF AMERICA, ...Washington, D.C., EXHIBITOR. Naval Engineering Experiment Station, Report C-3371-C: February 1950.

Samples of nine wrought and six cast aluminum alloys were exposed from December to June in sea water at 50-75 F flowing at the rate of 3 fps. The corrosion resistance of the wrought alloy 52S-1/2H (2.5Mg-0.25Cr) was excellent, and that of the wrought alloy 63S-T5 (0.4Si-0.7Mg) was fair. The other alloys had poor resistance and would be severely damaged by prolonged exposure to flowing sea water.

The wrought alloys 75S-T6 (1.6Cu-2.5Mg-5.6Zn-0.3Cr), 61S-T6 (0.25Cu-0.6Si-1.0Mg-0.25Cr), 4S-1/2H (1.0Mg-1.2Mn), and 3S-1/2H (1.2Mn) pitted to a depth readily measurable by depth gage or pointed micrometer. An alclad sample was penetrated to the 3S core, indicating that the coating alloy (72S) had comparatively low corrosion resistance. Two samples of 72S-0 (1.0Zn) showed no pitting on the surface but corrosion started at the edges and penetrated from one edge to the other. Evidence of intergranular corrosion was observed in the wrought alloys 61S-T6, 75S-T6, and 24S-T (4.5Cu-1.5Mg-0.6Mn).

Of the cast alloys, 220-T4 (10.0Mg) and 356-T6 (7.0Si-0.3Mg) were the most resistant to corrosion. Alloys B-214 (1.8Si-3.8Mg) and 214 (3.8Mg) were most susceptible to pitting attack. Alloys B-214, 220-T4, 356-T6, 43(5.0Si), and 195-T5 (4.5Cu-0.8Si) showed evidence of intergranular corrosion.

Test specimens were bolted at each end to a rectangular micarta rack. The racks were laid in a trough so that they were 2 in. above the bottom and 3 in. below the water surface. The direction of flow was normal to the longitudinal edges. The test site was Kure Beach, N. C.

18

Basil, J. L. THE RESISTANCE TO CORROSION OF CAST AND WROUGHT ALUMINUM ALLOYS IN SEA WATER. U.S. Naval Engineering Experiment Station, Report 4H(4)066918: October 1952.

A number of wrought- and cast-aluminum alloys were tested for corrosion resistance in natural sea water at Wrightsville Beach, N.C., and in brackish estuary water at Annapolis, Md.; results were compared with those of a similar test series carried out at Kure Beach, N.C. The effect of high water velocity was tested by rotating immersed specimens at high speeds. Resistance to impingement attack was determined by means of jet tests. Specimens were also exposed to quiet sea water, to sea water flowing at 10 fps, and to river water.

The aluminum alloys generally suffered considerably less corrosion damage at Wrightsville Beach than at Kure Beach, owing perhaps to the presence of corrosive decomposition products of marine organisms. At Wrightsville Beach, the wrought alloys 3S-1/2H (1.2% manganese) and 52S-1/2H (2.5% magnesium, 0.25% chromium) and the cast alloys 214 (3.8% magnesium) and 220 T4 (10% magnesium) were rated very good to excellent. Although they sustained considerable corrosion damage in the Kure Beach tests, they were superior to other aluminum alloys tested in the same location. The test results also emphasized the importance of insulating aluminum alloy assemblies from other metal systems.

19

Basil, J. L. RESISTANCE TO CORROSION OF SEVERAL WROUGHT ALUMINUM ALLOYS IN NATURAL SEA WATER. Navy Marine Engineering Lab. Report No. 040037A 4: AD- 43 667. March, 1954.

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Basil, J. L. and Rausch, M. W. SEA WATER CORROSION TEST OF ALUMINUM ALLOY PIPE. U.S. Naval Engineering Experiment Station, Evaluation Report 040037A 5: AD 56666. February 1955.

Results of sea-water corrosion tests on insulated pipe sections of 3S Alclad, 3S, and 52S aluminum alloys indicate that all three alloys have good resistance to general corrosion and corrosion-erosion but that the first two alloys are more resistant to pitting than is 52S. Pitting rates indicate a life expectancy of at least 10 yr for 3S and Alclad 3S pipe with a wall thickness of 0.133 in. exposed to water at a velocity of 10 ft per sec.

After 30 to 42 mo, the 3S aluminum pipe contained many small pits and a number of deeper pits with a maximum depth of 0.04 in. Alclad 3S pipe, after 12 to 24 mo, showed large shallow pits (0.16 to 0.019 in.) in the cladding material; there was no evidence of core pitting. 52S alloy pipes in test for 12 to 24 mo showed a number of scattered pits (maximum depth 0.041 in.) but no general roughening of the surfaces. All pipe showed corrosion-erosion beveling on the edges where the water entered. No intergranular corrosion was observed in any location.

The most serious disadvantage of aluminum alloys is that they are anodic to other metals and would corrode rapidly from galvanic attack if coupled to other metals in seawater piping. Their successful use would require either exclusion of other metals or complete insulation from them which probably would be impractical in piping systems on major naval vessels. Other problems are choice of fittings, especially valves, and a suitable method of joining.

21

Basil, J. L. SEA WATER CORROSION TEST OF ZINC, ALUMINUM, AND MAGNESIUM ANODES. U.S. Naval Engineering Experiment Station. Research and Development Report 910039A; AD 214703; 15 p. February 1959.

Anodes of high purity zinc, 95-5 Al-Zn alloy, and 91-6-3 Mg-Al-Zn alloy with 0.033 to 0.06% copper were tested as 5 in. diameter, 1/2 in. thick rotating discs at 1225 rpm, or a peripheral velocity of 27 fps, in sea water for 7 to 31 days. The severe corrosion-erosion conditions greatly accelerated anode consumption. Current outputs, however, were increased proportionately so that galvanic efficiencies were not reduced significantly over those in static tests. The aluminum alloy was the most corrosion-erosion resistant, zinc was next, and the magnesium alloy last. The metal loss for the aluminum alloy was about 50% greater than in the static test, while that of zinc was about 200% greater. In the magnesium alloys, neither copper content nor casting location (surface or interior) appeared to exert any significant effect.

The lack of effect of copper may be due to the modifying influence of the 0.20% manganese in the alloy, or to the rapid wastage of magnesium which masks the effect of minor constituents.

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Basil, J. L. THE CORROSION OF METALS AS A FUNCTION OF SEAWATER VELOCITY. Marine Engineering Lab. Report MEL A 72 64, AD 442 345L; 11 p., 1964.

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Basil, J. L. CORROSION OF MECHANICAL SEAL MATERIALS INDUCED BY COUPLING TO CARBON. Marine Engineering Lab., Report No. 117 64, AD 445 822L; 8 p., Aug. 1964.

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Beck, W. THE INTERNATIONAL CONGRESS OF FOULING AND MARINE CORROSION, JUNE 8-13, 1964. Office of Naval Research, London. TR C14 64, AD 450 804; 11 p., Sept. 1964.

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Beckner, C. F. MARINE FOULING AND CORROSION OF INSTRUMENTATION AT ARGUS ISLAND. Naval Oceanographic Office, Washington, D.C., Oceanographic Prediction Div. Report Informal Manuscript-0-55-65, AD 479 369L; 9 p., January 1966.

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Berry, W. E. REVIEW OF RECENT DEVELOPMENTS. CORROSION AND COMPATIBILITY. Battelle Memorial Inst., Defense Metals Information Center. Report AD-848 603; 4 p., Feb. 1969.

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Boeing Co. RESULTS OF 197 DAY EXPOSURE TO DEEP OCEAN ENVIRONMENT ON STRUCTURAL MATERIALS AND COATINGS. Report No. D2-125376-1, AD-826 888L; 48 p., April 1967.

Specimens of coated and uncoated metals, stressed metals, and plastics which were exposed for 6 months at a depth of 2500 feet in the Ocean off the California Coast. The subsequent evaluation of these specimens is the subject of this report.

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Bomberger, H. B., Cambourelis, P. J., and Hutchinson, G. E. CORROSION PROPERTIES OF TITANIUM IN MARINE ENVIRONMENTS. J. Electrochem. Soc., 101: 442-447, September 1954.

Data are presented on the behavior of commercially pure titanium and several common structural metals exposed to sea, industrial, and rural atmospheres for approximately 5 yr and to sea water at Kure Beach, N.C., up to 4.5 yr. Long-time tests designed to show susceptibility to

sea-water erosion, crevice corrosion, galvanic corrosion, pitting, stress corrosion, and corrosion fatigue had no noticeable effect on titanium metal. Titanium coupled to Inconel, silver, and Types 302 and 316 stainless steels had a negligible effect on the corrosion rates of these materials, but the corrosion rates of Monel, copper, low-carbon steel, and aluminum alloys were in some cases more than doubled by contact with titanium.

29

Booth, F. F. and Budd, M. K. CORROSION BEHAVIOUR OF TIG WELDS IN ALUMINUM SHIP-BUILDING ALLOYS. Welding & Metal Fabrication, 30: 483-486, December 1962.

Inert-gas tungsten arc (TIG) welded sheet specimens of the aluminum alloys N5, N4, H19 and H20 were subjected to 1- and 5-yr intermittent immersion in Brixham harbor, Eng., and to 4-mo immersion in a laboratory solution of 3% sodium chloride and 0.5% hydrogen peroxide. Alloy designations are those in B.S. 1470-1477.

Only welds in H20W were significantly corroded after 1 yr in sea water. After 5 yr, corrosion was negligible on N5-0, N5<sup>1</sup>/<sub>4</sub>H and N4<sup>1</sup>/<sub>2</sub>H. H19 in the W condition had a few broad pits; in the WP condition, attack was negligible. H20 in the W condition had deep pits in the heat-affected zone; in the WP condition, there were a few broad shallow pits.

In the laboratory, there was severe corrosion near the weld on H19W and H20W specimens but only slight pitting remote from the weld on H19WP and H20WP. N4<sup>1</sup>/<sub>2</sub>H was almost unaffected, but N5-0 showed deep attack at the weld-to-parent-metal interface.

It is concluded that aluminum-magnesium alloys are the best for welded marine applications and that aluminum-magnesium-silicon alloys are good if fully heat-treated. Painting the latter alloys is advisable for severe applications but is not always necessary. Marine fouling has negligible effect on corrosion. The laboratory test is more aggressive than 5-yr exposure in sea water and predicts service behavior well.

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Booth, F. F., Latimer, K. G., CORROSION BEHAVIOR OF ALUMINUM-TO-STEEL JOINTS WITH SPECIAL REFERENCE TO ALUMINUM SUPERSTRUCTURES ON SHIPS. In: Proceedings 2nd International Congress on Metallic Corrosion, New York, N.Y., March 11-15, 1963, p. 780-788

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Boyd, W. K. CORROSION IN DEEP-OCEAN AND RELATED ENVIRONMENTS. U.S Government Research and Development Reports, 40: No. 11: p. 28, June 5, 1965. PB-167 126.

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Brooks, R. E. CORROSION DESIGN IN THE MARINE APPLICATION OF ALUMINUM ALLOY FLOODLIGHTS. Corrosion, 16: No. 2: 41T-42T, Feb. 1960.

33

Brouillette, C. V. CORROSION RATES IN SEA WATER AT PORT HUENEME, CALIFORNIA, FOR SIXTEEN METALS, JULY 1951-JANUARY 1954. Naval Civil Engineering Lab. Rept. No. NCEL-TN-194, AD- 81 212: 26 p., Oct. 1954.

34

Brouillette, C. V. CORROSION RATES IN PORT HUENEME HARBOR. Corrosion, 14: 16-20, August 1958.

The corrosion rates of 16 metals and alloys were determined over a period of 30 mo total immersion in the sea water at Port Hueneme, California. Lead evidenced the least attack and magnesium alloys the most. Corrosion rates in the harbor at Port Hueneme where maximum flow rate is only about 0.2 ft per sec appear to be typical of the sea water along the California Coast, but were aggravated to some extent by marine growth. Pitting was a major factor in the corrosion of aluminum, stainless steel, and Monel. Clad aluminum (2024) showed less corrosion than any of the other aluminum group specimens. Deep pitting was prevented by cathodic protection provided by the cladding to the aluminum alloy substrate. Aluminum bronze and phosphor bronze corroded very slightly (about 0.5 mil per yr) and without pitting. Manganese bronze and Naval brass showed a similar corrosion pattern, but corrosion rate was about 1.1 mils per yr. Pitting on Monel was heavy particularly under areas of marine growth. Copper corrosion was confined almost entirely to panel edges with little attack on the flat surfaces. This was attributed to differences in temper at the edges caused by cutting from sheet stock. Low carbon steel corroded rapidly (6.8 mils per yr average with initial rates as high as 7.5 mils per yr).

35

Brouillette, C. V. CORROSION RATES OF URANIUM ALLOYED STEEL IN MARINE HYDROSPACE. Naval Civil Engineering Lab. Rept. No. NCEL-TN-950, AD-829 844: 23 p., Feb. 1968

Corrosion rates in the 3 hydrospace environments were primarily controlled by the dissolved oxygen concentrations and to a lesser extent by temperature. Segrega-

tion of uranium in the steels, which possibly could have occurred during production, could not be detected. Profuse micro-pitting over the surface of the uranium alloyed stainless steel was attributed to the uranium. Corrosion rates of steel in deep ocean were low.

36

Brown, B. F., Waldron, L. J., Peterson, M.H. CORROSION AND CATHODIC PROTECTION OF UNDERWATER SURVEILLANCE SYSTEMS - A GENERAL REVIEW OF THE PROBLEM. Naval Research Lab. Report No. NRL-MR-1436, AD-635 765: 10 p., June 1963.

A general review of the problem of corrosion of metallic assemblies for underwater surveillance is given, based on two years observing deep sea corrosion and on extensive technical discussions with personnel in contractors' plants and in Naval Activities having cognizance over surveillance systems. Recommendations to minimize corrosion failures in such systems are given.

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Brown, B. F., Lennox, T. J., Peterson, M. H. Smith, J. A., Waldron, L. J. INTERIM REPORT OF PROGRESS ON MARINE CORROSION STUDIES. Naval Research Lab. Report MR 1549, July 1964.

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Brown, B. F., Lennox, T. J., Newbegin, R. L. Peterson, M. H., Smith, J. A., Waldron, L. J. MARINE CORROSION STUDIES, DEEP OCEAN TECHNOLOGY, STRESS-CORROSION CRACKING, CATHODIC PROTECTION, SECOND INTERIM REPORT OF PROGRESS. Naval Research Lab., NRL Memo Report 1574, Nov. 1964.

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Brown, B. F., Forgeson, B. W., Lennox, T. J., Lupton, T. C., Newbegin, R. L., Peterson, M. H., Smith, J. A., Waldron, L. J. MARINE CORROSION STUDIES. STRESS-CORROSION CRACKING, DEEP OCEAN TECHNOLOGY, CATHODIC PROTECTION, CORROSION FATIGUE. Naval Research Lab., Third Interim Report of Progress, NRL Memo Report 1634, July 1965.

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Brown, B. F. HANDBOOK OF OCEAN AND UNDERWATER ENGINEERING. San Francisco, McGraw-Hill Book Company, p. 7-2 - 7-11, 7-26,- 7-30. 1969.

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Brown, B. F. A PERSPECTIVE VIEW OF DATA ON LOCALIZED CORROSION FOR THE MARINE DESIGNER. Marine Technology Society Journal, 3: No. 6: 67-69; Nov/Dec 1969.

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Brown, B. F., CORROSION IN THE MARINE ENVIRONMENT. In: Marine Technology 1970. Vol. 2: 1225-1231, 1970.

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Bulow, C. L. CORROSION AND BIOFOULING OF COPPER-BASE ALLOYS IN SEA WATER. Trans. Electrochem. Soc. 87: 319-352, 1945.

Slight modifications of the composition of copper alloys will in many cases greatly affect their corrosion resistance in unpolluted flowing sea water and their resistance to biofouling by macroorganisms.

ASTM tension specimens were carefully annealed, cleaned, analyzed, weighed, measured, and arranged in corrosion test racks. The two main groups studied were (1) copper-zinc and modified copper-zinc alloys and (2) copper-base alloys.

The specimens were exposed to flowing sea water (60 - 90 cm per sec) at Kure Beach, N.C. for periods of 6 and 12 mo at a temperature ranging from 2 to 30 C. After a few months exposure, all specimens were covered with slime. Some showed excessive biofouling by relatively large marine flora and fauna. The addition of small percentages of aluminum, arsenic, and iron to certain compositions resulted in marked increase of fouling.

Addition of small amounts of aluminum to some copper alloys increased the resistance to impingement corrosion, while arsenic or tin had the opposite effect on muntz metal. Of copper-zinc alloys those with 66% copper or 80 - 85% copper were most resistant to corrosion.

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Bulow, C. L., USE OF COPPER BASE ALLOYS IN MARINE SERVICES. Naval Engineers Journal, 77: No. 3: 470-482, June 1965.

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Butler, G. CORROSION AND ITS PREVENTION IN WATERS. London, Leonard Hill, 254-258, 1966.

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Central Dockyard Lab. Portsmouth, England. ALUMINUM SILICON BRONZE, EVALUATION FOR MARINE SERVICE. Report No. C.D.L. ACC/N247/69, AD-865 186: 10 p., 1969.

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Clarkin, P. A., and Bever, M. B. CORROSION RESISTANCE OF CARBO-NITRIDED STEEL. Metal Progress, 66 :No. 6: 108-109, December 1954.

The corrosion resistance of carbo-nitrided

steel was determined by total immersion in aqueous 3% sodium chloride solution and in fresh flowing sea water. Comparison tests were run on carburized specimens. The specimens were of normalized A.I.S.I. 1018 steel, surface ground and case hardened at 1400-1700 F in atmospheres containing 3-5% methane and 0-15% ammonia. Carbo-nitriding at low temperatures and with high ammonia concentrations resulted in the formation of a layer of carbon-nitrogen-iron compounds at the surface of the steel. Four specimens, each with a surface of 0.12 sq dm, were immersed simultaneously for 2-4 days in 8 liters of salt solution at  $30.0 \pm 0.5$  C aerated with 400 ml air per min per liter. Three series of specimens each with a surface area of 0.3 sq dm were exposed for 21-133 days in sea water moving at 1-2 ft per sec.

Plain carbon steel carbo-nitrided under conditions which did not lead to compound formation, corroded in aqueous sodium chloride solution at the same rate as carburized steel. Wide variations in the carbonitriding conditions and tempering had no appreciable effect on the corrosion behavior in the salt solution, but the presence of a compound layer cut the corrosion rate by about one half.

The sea-water tests, which were carried to the point of complete penetration in some specimens, suggested that under such extreme conditions the compound layer may be undesirable. In the sea water a heavy calcareous deposit formed on carbonitrided specimens having a compound layer on the surface, and no deposit or only traces formed on cases without the compound layer. This deposit was attributed to the fact that the surface is cathodic to the underlying metal; once such a case is penetrated, corrosion is accelerated by galvanic action between the core and the remaining case. However, for applications which require a case having both moderate hardness and moderate resistance to corrosion, e.g., in sodium chloride solution, carbo-nitriding under conditions which produce a compound layer at the surface should be considered.

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Cleary, H. J. ON THE MECHANISM OF CORROSION OF STEEL IMMERSSED IN SALINE WATER. First Annual Offshore Technology Conference. Vol. 1. Preprints, Held in Houston, Tex., May 18-21, 1969 : 375-388, 1969.

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Cordova, H., I., Kubose, D. A. EROSION-CORROSION OF HAYNES-25 ALLOY; RADIOACTIVE TRACER TECHNIQUES. Naval Radiological Defense Lab. Report No. USNRDL-TR-67-142, AD-663 566: 25 p., Aug. 1967.

The erosion-corrosion caused by the washing of a mixture of seawater and ocean-bottom material across a specimen of haynes-25 at ambient room temperature was studied with radioactive tracer techniques. The results obtained under the conditions of this study showed that the corrosion rate in such an environment increased 4 orders of magnitude over that observed in seawater alone.

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Cotton, J. B., and Downing, B. P. CORROSION RESISTANCE OF TITANIUM TO SEAWATER. Inst. Marine Engineers Trans., 69: No. 8: 311-319, 1957.

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Cox, F. G. THE CORROSION RESISTANT PROPERTIES OF ZIRCONIUM. PART 1 AND 2. Corrosion Prevention and Control 5: 39-42 April 1958, 46-48 June 1958.

A review is presented of the corrosion-resistant properties of zirconium with reference to various mineral acids, organic acids, alkalis, sea water, salt spray, inorganic salt solutions, miscellaneous reagents, and high temperature water and steam. General corrosion data are presented in tabular form.

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Crisci, J. R., Foster, M. L. DETERMINATION OF MECHANICAL PROPERTIES AND CAUSES OF FAILURE OF AUTEC - TOTO II DEEP SEA MOOR WIRE ROPE. Naval Applied Science Lab. Report No. NASL-930-44-PR-3, AD-840 610L. 26 p., Sept. 1968.

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Cuthbertson, J. W. THE RESISTANCE TO CORROSION BY SEA-WATER OF SOME  $\alpha$ -TIN AND  $\alpha$ -TIN-ALUMINUM BRONZES. J. Inst. Metals, 72: 317-342: 1946.

A study was made of the resistance to impingement corrosion, deposit attack, and simple immersion corrosion of tin and tin-aluminum  $\alpha$ -bronzes in the presence of sea water. It was shown that resistance to impingement corrosion demands primarily a high tin content, not less than 10%. An additional 1% of aluminum does not significantly affect resistance to impingement corrosion but improves resistance to other types of corrosion. Ternary bronzes containing 8% tin, the minimum amount for safety, require aluminum in order to resist impingement attack.

Aeration of the sea water is found to increase the rate of deposit and general attack of all the bronzes but does not significantly alter the order of corrodibility. The average rate for bronzes, under these conditions, is 20 - 40 mg per

sq dm per day. However, the more resistant bronzes are superior to cupro-nickel (rate 35 - 45) and aluminum brass (rate 25) under the same conditions.

A simple prefilming process has been developed which can improve the resistance of the bronzes to impingement and general corrosion. Its usefulness is limited under deposit attack.

Comparative tests on alloys prepared by normal methods of casting and from degassed melts and on materials having variable and controlled grain-size have established the importance of homogeneous structure and fine grain size in combatting impingement attack.

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Danek, G. J., Basil, J. L. SEA-WATER CORROSION BEHAVIOR OF Al-Cu-4M CU ALLOY. Navy Marine Engineering Lab. Report No. 113 64; AD-446 415L: 14 p., Aug. 1964.

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DeLuccia, J. J. and Taylor, Edward. EVALUATION OF METALLIC MATERIALS EXPOSED TO THE DEEP OCEAN ENVIRONMENT AT 5,640 FEET FOR 123 DAYS. Naval Air Engineering Center, Report No. NAEC-AML-2132: 72 p., June 1965.

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DeLuccia, J. J. . EVALUATION OF METALS IN DEEP OCEAN ENVIRONMENTS. Metals Protection. No. 5: p. 49-51, Aug. 1966.

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DeLuccia, J. J. Piland, J.A., CORROSION OF LIGHT ALLOYS IN DEEP OCEAN ENVIRONMENTS. Naval Air Development Center, Aero Materials Dept. Report No. NADC-MA-6946; AD-865 586L: 59 p., Feb. 1970.

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DeLuccia, J. J. METALLIC CORROSION IN THE DEEP-OCEAN ENVIRONMENT, SIX MONTHS AT 2,340 FEET. Naval Air Development Center, Aero Materials Dept. Report No. NADC-MA-6868; AD-848 907L: 73 p., Jan. 1969.

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DePalma, J. R. MARINE FOULING AND BORING ORGANISMS IN THE TONGUE OF THE OCEAN, BAHAMAS-EXPOSURE II. Naval Oceanographic Office, Report No. IMRO 64 62; AD-447 263: 8 p., Oct. 1962.

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DePalma, J. R. AN ANNOTATED BIBLIOGRAPHY OF MARINE FOULING FOR MARINE SCIENTISTS AND ENGINEERS. Journal of Ocean Technology, Vol. 2: No. 4: 33-44, July 1968.

The annotated bibliography was compiled to provide information and guidance to the marine scientist or engineer who must contend with those animals and plants which attach themselves to man-made underwater objects, i.e., fouling organisms. The references selected for this bibliography are those which help answer one or more of the following questions: What kind of fouling can one expect to find in various parts of the world; what are the factors which tend to promote or discourage the settlement and growth of fouling organisms; and What are the effects of this settlement and growth on the performance of coatings, sensors, and hardware.

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Eastwood, L. W., Fink, F. W., Davis, J. A. THE RELATIVE CORROSION RESISTANCE OF MAGNESIUM ALLOYS IN SALT WATER. Light Metal Age, 4: No. 4: 16-19, 1946.

Magnesium alloys of high purity, having 0.001% iron or less, have markedly improved resistance to salt-water corrosion regardless of their zinc content. With iron contents near 0.015%, representative of commercial purity, none of the alloys regardless of zinc content can be regarded as resistant to salt water corrosion. Therefore the use of high zinc alloys for their supposed resistivity to this type of corrosion is questionable.

Four types of alloys were tested. Two were German alloys of commercial purity with zinc contents of approximately 0.4% and iron contents ranging from 0.005 to 0.015%. The other two were American commercial types containing 2 and 3% zinc and 0.005 - 0.022% iron. High purity samples of these last two alloys, specially prepared for these tests, were also studied along with a third type containing approximately 1% zinc. Iron content of these high purity samples ran as low as 0.001%. The alloys were subjected to various heat treatments, aging, and quenching conditions.

In the heat treated and aged condition all four alloys of commercial purity appeared to have similar resistance to salt water, but before aging the alloys containing 0.4% zinc had slightly higher corrosion rates than those containing 2 or 3% zinc. All of the samples regardless of zinc content or purity had, in general, high resistance to atmospheric corrosion.

Previous work has indicated that although there is some decrease in the salt water corrosion rate of magnesium alloys containing up to 3% zinc, the major benefit of zinc addition is obtained at a level of 0.5% without sacrificing amenability of the

low-zinc alloys to heat treatment, or accenting their susceptibility to micro-porosity.

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Eichhorn, K. THE RESISTANCE TO CORROSION OF SEA WATER PIPING MADE OF COPPER AND COPPER ALLOYS. Werkstoffe u. Korrosion, Vol. 8: 453-456, August/September, 1957.

In German with English summary.

The choice between unalloyed copper and copper alloys for sea water piping on ships is determined mainly by the rate of flow. At low velocities, unalloyed copper has good resistance to corrosion due to its positive potential and the ability to form a protective layer ranging from a monomolecular thickness to 100 A. Where construction and operating conditions permit its use, 99.25 and 99.5% copper, free of oxygen with 0.3 to 0.5% arsenic should be used. Under normal conditions, flow rates of 1.8 m per sec for pure copper and 2.1 m per sec for copper containing arsenic are considered safe. Sea water impurities, deposits, or increased turbulence at pipe connections can cause local breakdowns of the protective layer at nominal velocities as low as 1.4 m per sec, leading to erosion of the pipe wall and eventually to anodic disintegration of the bare metal spots.

Lines made of copper-nickel alloys containing 5% nickel, approximately 1% iron and 0.5% manganese, or of 2% aluminum brass are considerably more durable than those of unalloyed copper, especially at the higher velocities. The latter forms an erosion resistant layer in sea water and its permissible flow rate is 4.6 m per sec, twice as high as that of unalloyed copper. Forming properties (hot and cold) of the alloys are similar to those of pure copper. Pipes of large diameters may be made; connections are welded or brazed as usual without difficulties. For brazing aluminum brass, silver solder is preferred.

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Evans, U. R. METALLIC CORROSION, PASSIVITY, AND PROTECTION. New York, Longmans, Green & Company, 1948.

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Ferrara, R. J. CORROSION OF BALL VALVES IN SEAWATER SERVICE. Naval Ship Research and Development Center. Rept. MATLAB-173/68, AD-841 332L: 33p., Sept. 1968.

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Fifer, D. E. SOME ASPECTS OF MARINE CORROSION AND ITS PREVENTION.

Australasian Corrosion Engineering, 6: No. 7: 15-20, July 1962.

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Fink, F. W. METALS FOR SEA WATER SERVICE. Ind. Eng. Chem., 52: No. 9: 70-A-71A, 73A, Sept. 1960.

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Fink, F. W. METAL CORROSION IN SALINE WATERS. Battelle Technical Review, 12: No. 9: p. 5-8, Sept. 1963.

68

Fink, F. W., Fuller, R. G., Nowacki, L. J. NAVIGATIONAL BUOY CORROSION AND DETEIORATION. In: Congres International de la Corrosion Marine et des Salissures, Cannes, France, June 8-12, 1964, Proceedings. p. 77-82, 1965.

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Fink, F. W. ALLOYS FOR SEAWATER CORROSION. Materials Protection, 6: No. 5; p. 40-43, 1967.

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Fink, F.W., Boyd, W. K. THE CORROSION OF METALS IN MARINE ENVIRONMENTS. Columbus, Ohio, Bayer & Co., 1970.

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Fischer, E. MICROBIOLOGICAL CORROSION: DEEP SEA. Naval Applied Science Lab. Rept. No. NASL-TM-2: AD-814 136L. 18p., Aug. 1965.

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Fleetwood, M. J. NONFERROUS METALS FOR OCEAN ENGINEERING. Werkstoffe u. Korrosion, Vol. 21: 267-273, 1970.

Following a comparative survey of the corrosion behavior of various nonferrous metals in sea water the author deals with the individual variables (flow rate, water depth, aeration) and the mechanical requirements such metals have to meet. Possible applications of Cu and Ni alloys are listed in this context, reference is made to recently developed alloys: weldable CuNi casting alloys, high strength CuNi alloys for use in sea water at high flow rates, high strength NiCrMo alloy for ropes which even during extended exposure to sea water must not lose their strength nor be susceptible to crevice corrosion.

73

Forgeson, B. W., Southwell, C. R., and Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 3. UNDER-WATER CORROSION OF TEN STRUCTURAL STEELS. Naval Research Laboratory, Report 5153: 24p., August 1958.

Structural steels (9 by 9 by 1/4 in. panels) of ten different compositions were exposed in the Panama Canal Zone for 8 yr. Comparisons are made between the severity of corrosion in the natural tropical environments of sea water mean tide, and sea water and fresh water continuous immersion. Results are correlated with similar corrosion tests made on the east and west coasts of the United States.

The corrosion of unalloyed low-carbon steel (Fed. Spec. QQ-S-741) in tropical sea water was of the same magnitude as temperate sea water corrosion at Kure Beach, N.C., and less than at Port Hueneme, Calif. After 8 yr at the three Panama environments, the maximum difference in the corrosion rates between continuous immersion in sea water, in fresh water, and at the mean tide exposure was 15%. Corrosion curves indicate that sea water corrosion proceeded at a linear rate, fresh water corrosion decreased with time, and sea water mean tide corrosion accelerated with time. Accelerated pitting attack on unalloyed low carbon steel with a millscale surface was evidenced only in the sea water immersion. In both the fresh water and mean tide exposures, pitting attack and weight loss on millscale, pickled, and machined surfaces were essentially equal at the end of 8 yr.

No significant difference was found in type or magnitude of corrosion between unalloyed and copper bearing low-carbon steels.

Additions of 3 and 5% chromium were beneficial in fresh water; pitting attack was slightly less and weight losses decreased more than 50% in comparison to unalloyed low-carbon steel. In sea water, however, the frequency of pitting on chromium steels was much greater. Weight loss of proprietary (3%) and AISI type 501 D (5%) chromium containing samples exceeded that of unalloyed steel by 63% and 30%, respectively.

74

Forgeson, B. W., Southwell, C. R., and Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 3. UNDERWATER CORROSION OF TEN STRUCTURAL STEELS. Corrosion, 16: 87-96, March 1970.

Corrosion of ten structural steels exposed to tropical sea and fresh waters was evaluated following an 8 yr exposure period.

The corrosion of unalloyed low carbon steel in Panama tropical sea water is the same magnitude as temperate Sea water corrosion at Kure Beach, North Carolina and less than at Port Hueneme, California. The profuse

marine growth in Panama may have afforded some protection.

After 8 yr, there was a maximum of 15% difference in the corrosion rates of unalloyed low carbon steels at the three environments in Panama - sea water immersion, fresh water immersion, and sea water mean tide. However, the shapes of the curves for these exposures indicate that sea water corrosion is proceeding at a linear rate, fresh water corrosion is steadily decreasing with time, and mean tide corrosion is accelerating. It is emphasized that short term tests would have given erroneous results. Unalloyed low-carbon steel with a mill scale surface showed accelerated pitting attack only in sea water immersion. Pitting attack and weight loss on millscale, pickled, and machine surfaces were essentially equal after 8 yr in both the fresh water and mean tide exposures.

No significant difference in type or magnitude of corrosion was found between copper-bearing steel and unalloyed low carbon steel in any of the three Panama locations.

The inclusion of 2 and 5% nickel in structural steel did not increase corrosion resistance in fresh water or at mean tide. In sea water, the nickel addition accelerated both weight loss and pitting-type corrosion attack.

Addition of 3 or 5% chromium improved corrosion resistance of panels immersed in fresh water. Pitting attack was slightly less and weight loss more than 50% less than for unalloyed low carbon steel. However, in sea water, although the severity of pitting was about the same in all three steels, the pitting frequency was much greater on chromium steels. Weight losses of 3 and 5% chromium steel exceeded that of the low carbon steel by 63 and 30%, respectively. In mean tide exposure, weight losses of the three steels were the same but pitting attack on the chromium steel was double that of mild steel and immeasurably higher in frequency.

Proprietary low-alloys steels in general were not more resistant to underwater corrosion than mild unalloyed steel and for certain conditions they were appreciably less resistant.

75

Forgeson, B. W., Southwell, C. R. and Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 5. STAINLESS STEELS. Naval Research Laboratory, Report 5517: 20 p., Sept. 1960.

Over a period of 8 yr, six stainless steels (AISI No. 410, 430, 301, 302, 321) were exposed to underwater and atmospheric environments in the Panama Canal Zone. In sea water, stainless steels were inferior to phosphor bronze and to structural steels. They were severely pitted during sea water immersion; mean tide produced one fourth to one tenth the pitting of continuous immersion. The greater pitting attack in tropical than in temperate areas may result from heavy marine fouling. These steels are not recommended for sea water service where perforation of structure is a consideration. When submerged in fresh water, stainless steels were practically unattacked. They were superior to ordinary steels and equal to phosphor bronze. Tropical atmospheres appear to be no more corrosive to stainless steel than temperate climates; the marine were slightly greater than the inland effects. However, precautions should be taken to eliminate cracks where passivity-destroying agents could accelerate pitting attack.

76

Forgeson, B. W., Southwell, C. R. and Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 5 - STAINLESS STEELS. Corrosion, 17: No. 7: 97-104, July 1961.

77

Forgeson, B. W., Waldron, L. J. ABYSSAL CORROSION AND ITS MITIGATION. PART II. RESULTS OF A PILOT TEST EXPOSURE. Naval Research Laboratory, Rept. No. NRL-MR-1383: AD-296 545: 25p., Dec. 1962.

Abyssal corrosion and its mitigation. Results of exposure of various materials (metals and non-metallic materials) at several depths up to 500 ft in Tongue of the Ocean for 3-1/2 mos.

78

Geld, I. DEEP SEA CORROSION OF MACHINED ALUMINUM PLATE. Naval Applied Science Laboratory, Rept. No. NASL-940-33-TM-24: AD-840 677L: 6p., Oct. 1968.

79

Geld, Isidore, Acampora, Mario. CORROSION OF MACHINED ALUMINUM PLATES AT DEEP SUBMERGENCE. Naval Applied Science Lab. Rept. No. NASL-940-33-PR-6: AD-860 048L; 30p., Sept. 1969.

80

Godard, H. P., Booth, F. F. CORROSION BEHAVIOUR OF ALUMINIUM ALLOYS IN SEAWATER. In: Congres Internatinnal de la Corrosion Marine et des Salissures, Cannes, France, June 8-12, 1964, Proceedings. p.37-52, 1965.

81

Godard, H. P., Jepsoson, W. B., Bothwell, M. R., Kane, R. L. CORROSION OF LIGHT METALS. New York, Wiley, 1967.

82

Gordon, H. B. HOW METALS RESIST SEA WATER. Materials Engineering, 65: No. 5; p.82, May 1967.

Presents a brief discussion and a table showing relative sea water corrosion rates of over 50 common metals and alloys. The main purpose of the table is to give materials engineers and designers a tool for comparing the relative sea water corrosion resistance of materials. The table lists depth of corrosion in inches per year times 10<sup>4</sup>. These values were computed from measured weight loss.

83

Goya, H. A., Lai, M. G., Kubose, D. A., Cordova, H. I. SNAP FUELS AND CAPSULE MATERIALS: A COMPENDIUM OF USNRDL LABORATORY PROCEDURES FOR THEIR STUDY. Naval Radiological Defense Lab., Rept. No. USNRDL-TR-68-55: AD-835 167L: 47p, Feb. 1968.

84

Gray, K. O. PROPERTIES OF MATERIALS IN DEEP-OCEAN ENVIRONMENT. Naval Civil Engineering Lab., Rept. No. NCEL-TN-380: AD-489 585: 9 p., March 1960.

85

Gray, K. O. EFFECTS OF THE DEEP OCEAN ENVIRONMENT ON MATERIALS - A PROGRESS REPORT. Naval Civil Engineering Lab. Tech. Note N-446, July 30, 1962.

86

Gray, K. O. ENVIRONMENT OF DEEP OCEAN TEST SITES (NOMINAL DEPTH, 2000 FEET) LATITUDE 33 DEGREES 46 MIN N, LONGITUDE 120 DEGREES 37 MIN W. Naval Civil Engineering Lab. Rept. No. NCEL-TN-657: AD-461 145: 28p., Feb. 1965

NCEL has exposed specimens of a large number of construction materials on submersible test units (STU) in 5300 and 5800 feet of water. The purpose is to determine that materials are most suitable to withstand the effects of this environment. The environmental factors considered significant are presented. The sea water at these sites is uncontaminated and normal for this part of the Pacific Ocean. The particular depth at which the STUs are located places them in an environment with a relatively low dissolved oxygen concentration. In this area, the oxygen minimum zone is located at a depth between 1800 and 2800 feet with dissolved oxygen values

as low as 0.20 milliliters per liter. Measurements averaging from 1.26 to 1.50 milliliters of dissolved oxygen per liter of sea water, 2.53 to 2.40 C for temperature, and 34.56 to 34.59 parts per thousand for salinity were obtained from the near bottom waters at these two depths (5300 and 5800 feet).

87

Greenblatt, J. H. CORROSION OF MAGNESIUM ALLOYS CONTAINING IRON AND NICKEL. J. Applied Chem., 9: 401-405, August 1959.

Magnesium alloys containing either 200 ppm or 2% nickel were immersed in sea water and corrosion rates determined either alone or coupled to steel cathodes of various sizes inserted in plastic or steel blocks. Ratio of cathode to anode areas were varied from 1:1 to 50:1. Rates were determined by weight loss, rate of hydrogen evolution, and rate of recession of the metal surface of the imbedded magnesium plug.

For uncoupled alloys the corrosion rate was higher for the 2% nickel alloys than the iron alloys. The initial state was important. For both alloys, a hydrochloric etch gave a higher rate. Nitric acid gave low initial rates presumably because of tight oxide film formed.

Both alloys, coupled to steel cathodes, showed a decreased rate of corrosion, the decrease increasing with cathode size. This is attributed to formation of an oxide film over the alloy. Some but not all of the decrease could be accounted for by accumulation of hydroxyl ions which, even at small concentrations, favor film formation and maintenance. Initial pretreatment is important since a smaller current density is required to maintain a protective film than to form it. For cathode to anode areas of 10:1, the critical current density is at least 50 ma per sq cm.

88

Groover, R. E. ANALYSIS OF THE FAILURE OF THE AUTECH TOTO II DEEP SEA MOOR AND PERFORMANCE OF ITS CATHODIC PROTECTION SYSTEM. Naval Research Laboratory, Memorandum Report No. 1950: 40 p., Nov. 1968.

The report contains background information on the design and installation of a wire rope three-point deep sea moor which was originally coated with a bituminous substance and the critical areas protected with a magnesium galvanic anode cathodic protection system designed by the Naval Research Laboratory. The report also describes the failure of the moor after 4 1/2 years service and its subsequent

salvage, and presents the results of a study of the corrosion pattern, proposes the cause of failure, and evaluates the performance of the cathodic protection system. Recommendations are presented for the protection of future moors and for possible research directed towards the understanding and prevention of failure of wire rope structures in sea water under conditions of static stress and of fatigue.

89

Groover, R. E., Lennox, T. J., Jr., Peterson, M. H. MARINE CORROSION STUDIES: CHARACTERIZATION OF THE CORROSION BEHAVIOR AND RESPONSE TO CATHODIC PROTECTION OF NINETEEN ALUMINUM ALLOYS IN SEA WATER. Naval Research Laboratory, Memorandum Report No. 1961: 24 p., Jan. 1969.

The corrosion characteristics of nineteen structural aluminum alloys were studied in quiescent sea water. Some alloys were exposed with and without cladding, and others at more than one strength level for a total of twenty-six material conditions. The response to cathodic protection of all the alloys studied was also determined. The electrochemical potentials of the alloys were monitored during the experiment and a relationship was developed between the electrode potential and the corrosion characteristics of the alloys. These mean potential values were found to differ significantly in many instances from the electrochemical potential values determined by other investigators from laboratory measurements in sodium chloride-hydrogen peroxide solution. Cathodic protection from galvanic anodes was effective in reducing the corrosion damage to acceptable limits except edge attack was not eliminated on one of the high strength 7XXX series aluminum alloys.

90

Groover, R. E., Lennox, T. J., Jr., Peterson, M. H. CATHODIC PROTECTION OF 19 ALUMINUM ALLOYS EXPOSED TO SEA WATER - CORROSION BEHAVIOR. Materials Protection, 8: No. 11: 25-30, Nov. 1969.

Data are reported on the corrosion behavior and electrochemical potentials of 19 structural aluminum alloys in quiescent sea water. A relationship was developed between the electrode potential and corrosion severity. Cathodic protection from galvanic anodes was effective in reducing the corrosion damage to acceptable limits for most of the alloys studied.

91

Groover, R. E., Lennox, T. J., Jr., Peterson, M. H. MARINE CORROSION STUDIES:

THE CORROSION CHARACTERISTICS AND RESPONSE TO CATHODIC PROTECTION OF COPPER ALLOYS IN QUIESCENT SEAWATER. Naval Research Laboratory, Memorandum Report 2183: AD-718 310: 54 p., Oct. 1970.

The corrosion characteristics dealloying susceptibility, marine fouling characteristics, and the response to cathodic protection of seventeen copper alloys and unalloyed copper, which served as a control, were studied in quiescent seawater. Detailed examination after 735 days showed that several alloys in the unprotected condition had severely corroded either by deep localized attack or by dealloying. The corrosion rates were determined; on the unprotected specimens a maximum rate of 0.74 mils per year was observed. Cathodic protection from zinc anodes reduced the corrosion rate to essentially zero and prevented localized corrosion except in Naval brass and Muntz metal where metallurgical studies indicated that dealloying was not completely prevented. Histograms have been presented for the electrochemical potentials of each specimen, and a galvanic series for the copper alloys has been included. There was no correlation between the electrochemical potentials and the type or severity of corrosion. The resistance of the copper alloys to marine fouling varied widely. All unprotected specimens fouled to some extent, whereas the cathodically protected specimens were heavily fouled.

92

Groves, Don. OCEAN MATERIALS. Naval Engineers Journal, 80: No. 2: 185-203, April 1968.

93

Guilhaudis, André. THE RESISTANCE OF LIGHT ALLOYS TO MARINE CORROSION. Rev. aluminium, 29: 85-91, 127-133, 175-179, March-May 1952.

In French

To obtain accurate estimates of the corrosion resistance of metals exposed to sea water and marine atmosphere, laboratory tests must be supplemented by field tests. This was done at the St.-Jean-de-Luz Mediterranean coast and at Salin-de-Giraud Atlantic coast marine corrosion test stations. The following results were obtained from a 2-yr exposure of protected and unprotected pure aluminum and various aluminum alloys.

Corrosion of pure aluminum was most severe when exposed to sea-water spray, less severe when alternately immersed,

and least severe when continuously immersed in sea water. In general, corrosion resistance increased as the purity of the aluminum increased from 99.7 to 99.99%. However, alternately immersed 99.7 and 99.8% pure specimens showed pitting, whereas specimens exposed to spray were heavily tarnished but showed no pits.

An aluminum alloy containing 0.70% manganese, 0.32% iron, 0.27% silicon, and 0.055% copper showed no pits whether immersed continuously or alternately; when subjected to spray, it tarnished after 3 mo.

Aluminum alloys containing 3-5% magnesium were among the most resistant unprotected alloys. An A-G5 alloy containing 0.44% manganese, 5.15% magnesium, 0.16% iron, 0.13% silicon and 0.035% copper, heat-treated at 400 C, increased in tensile strength during the first 3 mo, but decreased thereafter, particularly during the first year. Its percentage elongation decreased only slightly during the first 6 mo, but more rapidly thereafter when exposed to seawater spray. When immersed continuously in the sea, however, elongation decreased rapidly during the first 6 mo, and increased again during the next 6 mo before decreasing gradually during the second year.

Aluminum-magnesium-silicon alloys of the A-SG type (1.26% silicon, 0.98% magnesium, 0.16% iron, and 0.01% copper) which frequently also contain manganese, were superior to A-G5 aluminum-magnesium alloys in salt-spray resistance and equivalent under continuous immersion, provided they were tempered at 530 C for 45 min and water-quenched. Additional annealing at 175 C for 3 hr made the A-SG alloys more susceptible to corrosion.

Aluminum-copper-magnesium alloys, particularly A-V4G, were among the less resistant alloys. They showed serious pitting, and, in thin gauges, they showed perforations in as short a time as 3 mo, especially when partially annealed.

Because rain washes off salt deposits, surfaces exposed both to spray and rain were less corroded than those exposed only to spray. In contrast to most alloys tested, A-V4G corroded more severely when immersed constantly than when alternately immersed. In general this alloy should be protected when in contact with sea water. Provided it is thick enough, A-V4G can be used unprotected when exposed to spray.

Aluminum-zinc-magnesium-copper alloys of

the A-Z8GU type (8.49% zinc, 2.65% magnesium, 1.66% copper 0.34% iron, 0.25% chromium, 0.13% silicon, and 0.10% manganese) behaved essentially like A-V4G aluminum-copper-magnesium alloy. They showed local pittings and perforations when immersed, especially in the annealed condition, and almost greater losses in elongation than A-V4G under salt spray.

Plating with 99.5% pure aluminum or aluminum-zinc alloys A-Z3 provided good protection for both A-U4G and A-Z8GU alloys. The plated alloys showed increased resistance to both spray and permanent immersion. After the 2-yr immersion, the tensile strength of A-Z8GU plated with A-Z3 only dropped from 56.9 to 51 kg per sq mm, while its elongation dropped from 10.4 to 7.6%. After 2-yr seawater spray, plated A-V4G (Vedal) retained a strength of 39.5 kg and an elongation of 21%, compared with 34 kg and 10% respectively, for nonplated A-V4G. Comparative data on the seawater resistance of copper, nickel, tin, zinc, ordinary and stainless steels, and brass confirmed the merits of aluminum, aluminum-manganese, aluminum-magnesium, and aluminum-magnesium-silicon alloys, and of plated A-U4G and A-Z8GU alloys.

94

Guilhaudis, A. LIGHT METAL ALLOYS EXPOSED TO MARINE ATMOSPHERE. Corrosion et Anti-corrosion, 10: 80-85, March 1962.

In French

Corrosion tests on aluminum alloys at Salin-de-Giraud, Biarritz and Saint-Jean-de-Luz experiment stations are described. At Salin-de-Giraud, samples were exposed on a raft mounted on cylindrical floats, and large enough to accommodate vertical frames containing 400, 150 x 200 mm plates. The frames were partially immersed in water, so that half of the samples were exposed to marine atmosphere, half were immersed in sea water. The alloys for raft construction included A-G-3 (3% magnesium, 0.5% manganese) and A-G-5 (5% magnesium, 0.5% manganese): for the floats, A-5 ( $\leq$  0.5% iron and silicon) was used. Surfaces were protected by anodizing, primer and an antifouling top coat. No anodic oxidation was applied to the floats. The raft was constructed in 1946 and repainted in 1949 at which time it showed no corrosion, with the exception of rivets, around which the paint was completely deteriorated. Between 1949 and 1956, maintenance consisted in repairs of mechanical damages suffered during storms and in cleaning. The condition of the metals remained

generally good, despite partial deterioration of the paint. Corrosion spots appeared on some of the rivets and on floats. The latter were reconditioned by metallization or welding, and are still in service after 15 yr. At Biarritz, the test installation was constructed in 1952, and consists of a samples-supporting frame and a base, both made of A-G-3, resting on the sand. The construction becomes immersed in water during high tide and emerges at low tide. Base and frame are protected by a phosphatizing primer and a glycerophthalic top coat. After nearly 10 yr, there are only isolated corrosion spots on the metal surfaces. Samples of A-G-5 exposed for 5 yr show only a few small corrosion spots.

95

Hache, A. and Deschamps, P. STUDY OF SEA WATER CORROSIVITY. Corrosion et Anti-corrosion, 2: 134-140, July-August 1954.

In French

Using a new accelerated test for determining the corrosivity of salt solutions and natural sea water, the weight loss of an immersed steel specimen was shown to depend essentially on the volume and on the oxygen content of the solution.

Steel samples were immersed for short (1-24 hr) and medium (1-15 days) periods of time in various volumes of a 3% sodium chloride solution and of a filtered, stabilized natural sea water. The progress of corrosion was followed by determining colorimetrically with 1,10-phenanthroline the amount of iron dissolved.

For samples having a surface area of 1 sq dm and immersed for periods up to 24 hr, a constant corrosion rate during the entire test was obtained only if the volume of salt solution or sea water equaled or exceeded 4 liters. Otherwise, the depletion of oxygen in solution stifled the corrosion. To maintain a constant corrosion rate for several days, impractically large solution volumes would be required. It is hoped that the method of short-time immersions in adequate volumes of water can be adapted to the study of seasonal changes in the aggressiveness of natural sea water toward steel.

96

Hache, A., Barriety, L. and Debyser, J. THE EFFECT OF PHOTOSYNTHESIS ON THE CORROSION OF STEEL IN SEA WATER. Werkstoffe u. Korrosion, 10: 145-148: March 1959.

In German with English summary.

A linear relationship was found between the corrosion of steel and the oxygen content of sea water or sodium chloride solutions in which the metal was immersed. Seasonable variations in the properties of sea water were noted, especially the content of dissolved oxygen due to photosynthesis by algae.

97

Hache, A., Barriety, L., and Debysier, J. INFLUENCE OF PHOTOSYNTHESIS ON THE CORROSION OF STEEL IN SEA WATER. Corrosion et anti-corrosion, 7: 56-61, February 1959.

In French

Corrosion of steel in sea water tanks containing an abundant growth of algae was more extensive than in pure sea water. Laboratory and field tests were conducted to determine the possible role in corrosion of oxygen liberated in the process of photosynthesis. In laboratory experiments, pairs of 50 x 50 mm steel plates were immersed in a 3% solution of sodium chloride at 24 C; 5 to 30 mg oxygen/liter was introduced by bubbling the pure gas through the solution.

The rate of corrosion of the steel samples, determined gravimetrically, was directly proportional to the concentration of oxygen in the solution and, within the 6.5 to 8 range, did not depend on the pH. In field experiments, in which steel samples similar to the above were immersed in sea water tanks containing algae and in tanks containing pure sea water through which oxygen was bubbled, a direct relation was obtained between the oxygen content of the water and the rate of steel corrosion. At equal concentrations, photosynthetic and artificially introduced oxygen had the same effect on corrosion. Due to unfavorable weather conditions during the experimental period, the maximum concentration of the photosynthetic oxygen was only 20 mg/liter. The maximum concentration of the artificially introduced oxygen was 30 mg/liter. Corrosion rate values obtained in field experiments were corrected for a temperature of 24 C (5% for each degree difference), to make them comparable with the values obtained in laboratory experiments. At the same oxygen content, the corrosion rate in sea water was somewhat lower than in 3% sodium chloride.

98

Hache, A. STUDY OF THE CORROSION BEHAVIOR OF SOME STEELS EXPOSED AT DIFFERENT TEST STATIONS. Rev. Met., 59: 519-529, June 1962.

In French

Structural steels (of the type used in ship hulls), including 4 Thomas steels, 2 Martin steels, and 2 steels stabilized with 0.12% vanadium and 0.44% chromium, respectively, were subjected to corrosion tests involving immersion in sea water and/or exposure to the atmosphere at various locations.

Despite differences in the degree of infestation with marine organisms, immersion tests showed relatively small differences in the corrosion rates from one station to another, with average weight losses at the end of 4 yr ranging from 519 gm at Abidjan to 178 gm at Biarritz. In these tests, the behavior of all steels was practically identical. The relatively high rate at Abidjan can be related to the high water temperature, while the relatively low rate in Biarritz is apparently due to rust accumulation on the metal, made possible by the absence of underwater currents.

99

Hazard, P. M. HOW ENVIRONMENT AFFECTS OCEAN CABLES. Bell Labs. Record, 39: No. 3: 92-96, March 1961.

100

Hibert, C. L. ALUMINUM ALLOYS FOR MARINE USE. General Dynamics/Convair. Rept. No. ZM 658: AD-259 725: lv.: June 1961.

101

Holsberg, P. W., CORROSION STUDIES OF 10Ni-2Cr-1Mo-8Co STEEL. Naval Ship Research and Development Lab. Rept. No. NSDRL/A-8-438: AD-867 332: 27 p., March 1970.

102

Horne, R. A. PHYSICAL CHEMISTRY OF THE DEEP OCEAN ENVIRONMENT. Inc. Rept. No. TR-11: AD-462 328: Contract Nonr 4424 00: 23 p., May 1965.

This paper reviews the results of some simple experiments which we have performed in our Laboratory over recent years in a simulated deep ocean environment.

103

Hsieh, Wu-Yu, and Turkovskaya, A. V. CORROSION OF COPPER-NICKEL ALLOYS IN SEA WATER. Izvest. Vysshikh Ucheb. Zavenenii, Tsvetnaya Met. 4: No. 4: 145-148, 1961.

In Russian

The corrosion rates and electrode potentials in artificial sea water were determined for electrolytic copper, electrolytic nickel and for twelve copper-nickel alloys containing 4.75 to 59.1% nickel. Measurements were made in stationary and circulating water, with circulation speeds  $\leq 17.3$  m/sec.

Under all experimental conditions the corrosion rate of copper-nickel alloys decreased with increasing content of nickel, reached a minimum at approximately 20% and remained constant at higher contents. The corrosion rate was higher in circulating than in stationary water, and was related directly to the speed of circulation. The rate increased sharply above 8 m/sec. Correspondingly, the electrode potentials of the alloys became more positive with increasing nickel content, and were shifted toward more negative values by circulation of the electrolyte, the magnitude of the shift increasing in proportion to circulation speed. Under conditions of anodic polarization, the electrode potentials rose sharply at a nickel content of 20%, and changed little at higher contents. When the electrode potentials were measured under conditions of continuous removal of corrosion products from the surface (by means of a rotating carborundum disc), the potentials became more negative with increasing nickel content up to about 20%, and remained approximately constant at higher contents.

These results show that in copper-nickel alloys, a limit resistance to corrosion is reached at a nickel content of about 20%, and that the resistance to corrosion is due to increased passivation tendency at this nickel content.

104

Hutchinson, G. E., and Permar, P. H.  
CORROSION RESISTANCE OF COMMERCIAL PURE TITANIUM. Corrosion, 5: 319-325, Oct. 1949.

Titanium possesses outstanding resistance to corrosion in sea water, marine atmospheres, water-saturated chlorine, chloride salts, and strong oxidizing agents. Fouling organisms can grow on titanium surfaces but their presence does not encourage pitting or other types of corrosion.

Sample strips of metal were unaffected by a 120-day exposure either in the sea-spray test rack, 80 ft from the ocean, or in the marine atmospheric test lot, 800 ft from the ocean. Specimens totally submerged in sea water subject only to tidal fluctuation showed no pitting or crevice corrosion and negligible over-all attack; increasing the velocity of the water to 3 fps in a sea water trough had no effect.

Exposure for 30 days to impingement attack in an aspirator-type sea water jet of 12 fps velocity and 23.5 C average temperature caused no appreciable weight loss and no surface erosion or corrosion.

Data obtained with a high-speed galvanic tester indicate that titanium is near the bottom of a galvanic series of metals and alloys in sea water.

105

Hudson, J. C., and Stanners, J. F.  
THE CORROSION RESISTANCE OF LOW-ALLOY STEELS. J. Iron & Steel Inst., 180: 271-284, July 1955.

A systematic investigation was made of the effect of small amounts of alloying elements on the corrosion resistance of sixty mild steels in industrial atmospheres and in seawater over a 5-yr period. Laboratory spray tests also were conducted to compare reproducibility of results.

In general, low-alloy additions gave considerable reduction in atmospheric corrosion. The most resistant steels rusted at one third the rate of unalloyed mild steel during the first 1 or 2 yr of exposure. With longer exposure this inhibiting effect was even more apparent. The most useful of the alloying elements were chromium, copper, and nickel with aluminum and beryllium showing some advantage. On immersion in seawater, there was less improvement in resistance; under the stagnant conditions of flow used in these tests, the addition of 3% chromium to mild steel roughly halved its wastage by corrosion over a 5 yr period.

Carbon content within the range of 0.04-0.51% is not a major factor in the resistance of plain carbon steels to atmospheric corrosion. High carbon steels were less corrodible in an industrial atmosphere than low carbon steels but this position was reversed in seawater. The differences, however, were only about 20% in each case.

Heat treatment is not a major factor in determining the severity of corrosion of low alloy steel over long periods of exposure to air and sea water but it may have a pronounced influence in laboratory tests extending over a few weeks only.

There was little difference in the general corrosion of cast irons and plain carbon steels when immersed in sea water, although the former may be seriously weakened by local attack and graphitization. Laboratory tests of the intermittent spray

type yielded only fair correlation with the results of outdoor exposure, probably because the rusting of steels in the laboratory does not proceed sufficiently far for the difference in the properties of the rusts on the various steels to become fully operative.

106

Hunt, J. R., Bellware, M. D. OCEAN ENGINEERING HARDWARE REQUIRES COPPER-NICKEL ALLOYS. Navy Marine Engineering Laboratory, p. 243-275: 1967.

The copper-nickel alloys were developed early in this century to fill the need for marine materials more resistant to both quiet and moving sea water (velocity effects) than other copper alloys. They retain a high degree of the anti-fouling characteristics of copper. Nickel improves durability in sea water, and at the same time, imparts a high degree of fabricability found in few alloy systems. Over the years, these alloys have become available in the many forms required, with specifications having been established for plate, sheet, strip, rod, wire, pipe, tubes, castings, and welding electrodes. Copper-nickel offers the designer and user of the increasing array of ocean engineering hardware the opportunity to standardize and simplify many of his materials requirements with an alloy system of proven marine durability. The versatility of these alloys and their availability and fabricability in so many forms permits the use of a single alloy for various components and thus avoids problems of galvanic origin. Mechanical and corrosion properties, as well as welding and other fabricating procedures are listed and described. The why, when, where and how approach is directed towards both design and fabrication.

107

International Nickel Co., Inc. REPORT ON SPECIMENS REMOVED FROM SEA WATER TESTS AT KURE BEACH, N.C., MAY 1948. 23 p., July 1948.

This study was designed to indicate commercially significant differences in the corrosion of various metals in sea water.

Mild steel, 2% nickel steels, and various other low alloy steels, all with pickled surfaces, were immersed in 3 - 4 ft of sea water for 9.7 yr under conditions devoid of galvanic effects. Insignificant differences both in weight losses and pitting were found among the steels; but these steels, as a class, have some advantage over carbon steel with respect to pitting.

Panels of mild and high tensile steels welded with various electrodes were immersed for 1209 days, and a second identical series for 870 days. All welds satisfactorily resisted corrosion except Murex #80 and Fleetweld #5 welds on high tensile steel and Unionmelt welds on mild steel. There was no evidence of localized accelerated corrosion along the margins of the austenitic welds.

A mild steel plate was made up with four rows of countersunk rivets including those of SAE 2115 nickel steel, 2% nickel - 1% copper steel, carbon steel, and wrought iron. The plate was immersed in sea water for 10 yr and losses were measured by micrometer calipers. Behavior of nickel or nickel-copper steel rivets in carbon steel plates was much better than those of carbon steel or wrought iron. There was practically no attack on either button head or countersunk head; corrosion of the carbon steel around the alloy rivets was no greater than elsewhere.

Specimens of a killed carbon steel, two American steels containing 3% and 5% chromium, and two French steels, one containing 2% chromium - 1% aluminum and the other 3.7% chromium - 1.3% aluminum, were sandblasted; half were either tested in the unpainted condition or were painted with a coal-tar enamel and then immersed. The other half was given a passivating treatment and part of these exposed without paint and the remainder coated with the coal-tar enamel before immersion. One series was removed after 165-days exposure, the other after 351 days. The passivating treatment apparently did not improve corrosion resistance of any sample, but one coat of enamel was beneficial. All low alloy steels corroded similarly, and were superior to the killed carbon steel.

In a test to determine the effect of structure on corrosion, panels of killed carbon steel were exposed to sea water for 198 days. Panels which had been heat treated to produce a spheroidized carbide structure corroded almost twice as fast as those with a lamellar pearlite structure. Pitting occurred to the same extent on both.

Samples of several types of nitrided and unnitrided stainless steels were immersed for 178 days. The nitrided steel showed a relatively high over-all corrosion rate comparable with that of carbon steel. The unnitrided metal was bright but apparently more susceptible to pitting.

Nickel-antimony-lead bearing bronze was almost as resistant as the standard lead-tin alloy when exposed to sea water for 307 days. The nickel-antimony-tin-lead

type was inferior to both, corroding more rapidly and being more susceptible to pitting.

Pure hot-rolled zinc samples immersed for periods ranging from 186 to 1460 days corroded at a slightly greater rate than impure specimens.

108

International Nickel Co., Inc. TOUGH MATERIALS FOR TOUGH SERVICE. ALLOY DEVELOPED FOR CONDENSER TUBE AND OTHER CORROSION RESISTANT USES SHOWS NEGLIGIBLE ATTACK ON WELDED AND UNWELDED SAMPLES AFTER 11 YEARS IN SALT WATER. INCO 22 no. 2: 8 p., Summer, 1948.

Two samples of a 70/30 cupro-nickel alloy, one welded and one unwelded, were immersed in sea water for 11 yr. The welded sample was partly immersed for almost 5 yr in polluted harbor water at Newport News, Va., then exposed at Kure Beach, N.C. for an additional 6 yr in sea water flowing at the rate of 120 ft per min. The unwelded sample was immersed for 11 yr at Kure Beach. Results were identical for both; the corrosion rate was 0.0002-in. penetration per year. The 70/30 compound also resisted fouling by marine organisms, stress-corrosion cracking, pitting, and erosion, and was not susceptible to dezincification.

109

International Nickel Co., Inc. REPORT ON SPECIMENS REMOVED FROM SEA WATER TESTS AT KURE BEACH, N.C., MAY 1949. 30 p., October 1950.

Effects of minor constituents on sea water corrosion of 70:30 copper-nickel alloy. Alloys containing various percentages of zinc, iron, manganese, tin, chromium, and arsenic were exposed for approximately 10 yr at a depth of 3-4 ft in sea water flowing at a velocity of 1-2 fps. Corrosion rates, measured by weight loss and pitting, decreased considerably with prolonged exposure, regardless of minor constituents present. Zinc had little effect on weight loss but tended to aggravate pitting of iron-modified alloys; the zinc content should be kept at or below 0.5%. For service in low-velocity flow, the iron content need not be as high as for high velocity use, e.g., in condenser tubes. Some quantity of iron, however, is desirable, since a very low iron content led to relatively severe over-all attack. Under the given experimental conditions, as much as 0.9% iron can be used without increasing susceptibility to pitting. Manganese was slightly beneficial, especially in reducing pitting, in alloys in which the zinc

content did not greatly exceed the iron content. The main action of tin was to suppress a detrimental effect of 1% zinc. Chromium and arsenic by themselves did not show any important effects.

Zinc-coated steel. The life of a hot-dipped zinc coating was approximately 1 yr per ounce of coating weight when immersed in sea water flowing at a rate of 1-2 fps.

Behavior of Hastelloy C. In similar sea water exposures up to 10 yr, Hastelloy C, like Hastelloy A and B, corroded less in the rolled and sandblasted conditions than in the cast and ground conditions. Neither type specimen showed any pitting or crevice corrosion under bakelite washers used to insulate samples from the exposure rack.

Sea water tests on Stellite. Specimens immersed under similar flow conditions for approximately 7 yr showed crevice corrosion. Stellite was much less susceptible to pitting than to corrosion, but corroded slightly faster in the ground state than in the as-rolled condition with scale present.

Sea water tests on Illium. In 5-yr sea water exposure, Illium G corroded faster than Illium R, but did not pit. Illium R exposed without removing the hot rolling scale pitted on the surface at breaks in the oxide scale. This was probably caused by local galvanic action at the breaks with the scale being cathodic to the base alloy. Both this sample and a pickled Illium R sample corroded under the bakelite washers.

Behavior of Zincilate in sea water. Steel panels with four different Zincilate coatings were exposed approximately 1 yr at a depth of 3-4 ft and a flow rate of 0-4 fps. The Zincilate treatments did not prevent fouling but did reduce the corrosion rate considerably.

Behavior of low-alloy chromium and chromium-aluminum steels with various surface treatments. Painted and unpainted steels were passivated by immersing them in concentrated nitric acid for 5-6 min at room temperature, rinsing, immersing 10-15 min in boiling 3% potassium chromate-0.5% disodium phosphate solution, and drying. The treatment did not improve the corrosion resistance of the steels when exposed 2 yr to quiet sea water. One coat of Bitumastic B50 paint applied cold was beneficial. The four low-alloy steels tested, viz., two French steels, one containing 2% chromium and 1% aluminum, the other containing 3.7% chromium and 1.3% aluminum; and two American steels containing 3 and 5% chromium, respectively, corroded in

about the same way, all being superior to a killed carbon steel control.

Behavior of titanium-nickel-cobalt-silicon alloys in sea water. Ti-Ni-Co-Sil #10 and #54 corroded to about the same extent during a 1.5-yr exposure in quiet sea water. One specimen of the #54 alloy started to corrode around the edges and the other suffered severe attack on the surface, probably because of poor insulation at the fastening.

110

International Nickel Co., Inc. REPORT ON SPECIMENS REMOVED FROM SEA WATER TESTS AT KURE BEACH, N.C., MAY 1950. 36 p., February 1951.

A study was made of the corrosion of steel specimens in sea water. Unless otherwise stated the specimens were immersed at a depth of 3-4 ft in an intake basin at Kure Beach, N.C., where the tide rose and fell but had no definite flow.

Welded steel panels. One series of mild and high-tensile steel panels welded with various electrodes was immersed in flowing sea water for 1877 days; a second series was immersed in an intake basin for 1538 days. All the welds resisted corrosion satisfactorily except Murex #80 and Fleetweld #5 on high-tensile steel, and Unionmelt on mild steel, which seemed to be pitted. There was no evidence of localized accelerated corrosion along the margins of austenitic stainless steel welds.

Cast Iron and Type 2 Ni Resist welded with Ni Rod and R-29. Visual inspection of the welds after 671 days of exposure showed the welds to be resisting corrosion satisfactorily.

Rimmed steel. There was not much difference in corrosion resistance or susceptibility to pitting in samples from the butt core, middle skin, or top skin of ingots taken from the same heat. Specimens from the middle skin, however, corroded more and showed larger differences in thickness range than did the other specimens.

Copper steel and Types 316 and 304 stainless steel. Immersion tests lasting approximately 2 yr in both the intake basin and in sea water flowing at 0.4 fps showed that there was little difference in the performance of these alloys under the slightly different test conditions.

Rivets. Copper plates joined with steel rivets and steel plates joined with copper rivets were immersed for 14 mo. The steel rivets were completely corroded away from

the copper panel but the copper rivets in the steel plate were unaffected. Because of the favorable area relationships in the assembly of steel plates with copper rivets, the galvanic acceleration of the corrosion of the steel was negligible; where the reverse area relationship existed, the galvanic action of the copper on the steel was great.

Fine silver. Fine silver specimens, 4 by 12 in., were insulated by bakelite from Monel racks and immersed for 597 days in an intake basin, then for 317 days in sea water flowing at 0-4 fps, and finally reimmersed for 127 days in the flowing water. The corrosion rate varied during the three periods but the over-all corrosion was the same in both panels tested; the rate was uniform with time and was more severe in summer than in winter.

Special washers and zinc oxide to prevent crevice corrosion. Washers that had been vacuum-impregnated with Superla #8 wax and knurled to a depth of 0.010 in. on one side did not prevent crevice corrosion of austenitic steel in a 419-day immersion test. Washers were placed both with the knurled and smooth side next to the steel. Hi-Seal Plastic Jointing Compound, Hi-Seal Plastic Threading Compound, and Hi-Seal Plastic Sealing compound were applied under bakelite washers used to insulate specimens from Monel racks and fastenings. None of these materials satisfactorily prevented crevice corrosion in Type 430 stainless steel with #4 finish or Type 304 stainless steel. Hi-Seal Plastic Jointing Compound may be slightly superior. Zinc oxide smeared under the washer provided excellent protection from crevice corrosion for Type 304 stainless steel immersed for 92 days.

Glass-coated steel. Steel specimens were coated with glass, leaving a bare spot 0.25 in. square in the center of each side. After 470 days immersion, attack at the bare spots was less than on completely bare specimens. Crowding both the anodic and cathodic portions of the corrosion reaction into a relatively small surface tended to diminish rather than increase the rate of corrosion.

Synthetic rubber coatings. Panels coated with neoprene, Buna D hard rubber, and Thiokol were immersed for 2 yr in 3-4 ft of sea water flowing at 1-2 fps. None of the coatings prevented fouling. After 11 mo the Thiokol coating was crazed and at the end of 18 mo barnacles were cutting into it. After 2 yr the panels were removed from the flowing water and immersed to the same depth in the intake basin. At the end of 75-mo total exposure, the

neoprene and Buna S coatings were not damaged, although barnacle bases were on the surfaces. There were more barnacle bases on the Thiokol-coated specimen; the coating was gone from one corner and had been lifted along one edge. None of the specimens, however, were in much worse condition than when removed from the flowing water.

Effect of structure on the corrosion of killed carbon steel. Specimens of carbon steel having a spheroidized carbide structure corroded almost twice as fast during the first 6 mo as did specimens of the same steel having a lamellar pearlite structure. During the next year the spheroidized carbide structure corroded at a slightly faster rate than formerly but the lamellar pearlite structure corroded about 5 times the rate noted for the first 6 mo and about twice as fast as the spheroidized carbide specimen. During the third exposure period (322 days) the corrosion rate was appreciably reduced for specimens of both structures and although the spheroidized structure corroded at a faster rate, the lamellar structure still showed a higher total corrosion rate. Specimens of both materials were severely perforated at the end of the three periods totalling 891 days. During the first period of exposure, corrosion occurred in the decarburized zone of the lamellar pearlite specimen and during the next two periods progressed into regions not decarburized. Corrosion of the spheroidized structure proceeded into the decarburized zone during the entire test and hence showed no rapid acceleration of corrosion rate.

Bolts and nuts. Cast iron bars were bolted together with bolts and nuts made of cast iron, Ni Resist, Carson Cadillac, or steel and immersed for 517 days. Ni Resist showed superior corrosion resistance.

111

International Nickel Co., Inc., SUMMARY OF DATA COVERING EXPOSURE OF MANGANESE MODIFIED CHROMIUM NICKEL AUSTENITIC STAINLESS STEELS TO CORROSION BY SEA WATER AND SALT AIR. 10 p., June 1956.

Chromium-nickel and chromium-manganese stainless steels were immersed in flowing sea water (3 to 4 ft deep, 1 to 2 fps flow velocity) at Kure Beach, N.C. for 191 and 324 days. These alloys were also exposed for 1 to 9 yr to marine atmospheres 80 and 800 ft from the beach. The manganese additions varied from 4 to 20%.

All specimens showed severe localized corrosion by the salt water. Stainless steels

containing high manganese were less resistant than 18-8 stainless (types 302 and 304) although neither of the 18-8 alloys is considered satisfactorily resistant to salt water under complete and continuous immersion for prolonged periods. Copper powder-vaseline paste applied under the bakelite washers was not completely effective in preventing corrosion.

The marine atmospheric resistance of a chromium 18, nickel 4, manganese 4 was superior to that of an 18-8 stainless (Type 302) after 1 yr, but not after 9 yr in the 800 ft lot. After 5 yr exposure in the 800 ft lot, manganese-chromium alloys similar in composition to AISI Type 201 (chromium 18, nickel 4, manganese 6) were approximately equivalent to 18-8 (Type 304) stainless steel in corrosion resistance. Alloys of higher manganese content (9 to 10%), with and without nickel, were less resistant to this environment than stainless Type 304.

Exposure conditions were more severe at the Kure Beach 80 ft lot. With the exception of AISI Type 201, all of the manganese-chromium grades exposed at this location were less resistant than 18-8 (Type 304). The highest manganese content compatible with corrosion resistance in this environment was 9%. When nickel was added to the 9% manganese-chromium stainless steel, corrosion resistance was further reduced.

112

Janecka, Hans. BIO-DETERIORATION OF CENTER MATERIALS AND STRUCTURES IN THE MARINE ENVIRONMENT. A BIBLIOGRAPHY. National Academy of Science, National Research Council, Prevention of Deterioration Center. Report PDC 60 zDC 60 013, Rev. 1, AD-440 946: 82 p., Dec. 1963.

113

Jenkins, J. F., Reinhart, F. M. SEAL SYSTEMS IN HYDROSPACE, PHASE I - MECHANICAL INTEGRITY OF FLANGE SEAL SYSTEMS. Naval Civil Engineering Lab. Report NCEL-TN 999, AD-843 582L: Nov. 1968. Long-term effects of hydrospace on seals and gaskets are under investigation at NCEL. Phase I includes investigation of the mechanical integrity of fifteen seal systems by means of tests in pressure vessels. There was no seal extrusion or leakage of any of the configurations investigated. Long-term ocean exposures and cyclic loading of seal systems in pressure vessels are planned.

114

Jenkins, J. F., Reinhart, F. M. SEAL SYSTEMS IN HYDROSPACE, PHASE II. CYCLIC LOADING OF FLANGE AND HATCH SEAL SYSTEMS. Naval

Civil Engineering Lab. Report NCEL TN-1022, AD-684 080: March 1969.

Long-term effects of hydrospace on seals and gaskets are under investigation at NCEL. Phase II includes investigation of the effects of cyclic loading on fifteen seal systems by means of tests in pressure vessels. Fourteen of fifteen test systems withstood 20 pressure cycles to 5,000 PSI without leakage or visible seal damage. Long term ocean exposures of seal systems are planned.

115

Jenkins, J. F., Reinhart, F. M. SEAL SYSTEMS IN HYDROSPACE, PHASE III: EFFECTS OF LONG TERM HYDROSPACE EXPOSURE ON SEAL SYSTEM INTEGRITY. 189 DAYS AT 5,900 FEET. Naval Civil Engineering Lab. Report No. NCEL-TN-1072, AD-865 361: 48 p., Jan. 1970.

Long-term effects of hydrospace on seals and gaskets are under investigation at NCEL (Naval Civil Engineering Laboratory). Phase III includes the evaluation of fifteen seal systems and five metallic seal flange materials after exposure to the marine environment for 189 days at a depth of 5,900 feet in the Pacific Ocean.

116

Jones, R. E. DESIGN, PLACEMENT, AND RETRIEVAL OF SUBMERSIBLE TEST UNITS AT DEEP-OCEAN TEST SITES. Naval Civil Engineering Lab., Report No. NCEL-TR-369, AD-615 769: 92 p., May 1965.

Four submersible test units (STU'S) were emplaced, exposing specimens of various materials to the sea floor sediment and to the surrounding water for various time periods and at various depths. Emplacement of the four and the retrieval of one (after 4 months) are reported in detail, and the rigging and instrumentation systems are described. The heaviest STU emplaced so far weighed almost 7,500 pounds and supported about 2,400 specimens of 600 different materials. Emplacements were made at depths of 2,400, 5,600, and 6,700 feet. Operations and system performance are discussed and conclusions and recommendations are presented.

117

Keehn, P. A. BIBLIOGRAPHY ON MARINE CORROSION. Meteorological and Geostrophical Abstracts. Report No. Contrib-4: AD-821 559: 160 p., June 1967.

118

Khan, D. K., Mukherjee, D. P., and Bannerjee, T. SEA WATER CORROSION OF NICKEL AND OTHER METALS. N.M.L. Technical Journal, 8: p. 17-21, Nov. 1966.

The authors report some results obtained in initial studies at Digha, of corrosion of following materials by sea water under natural and laboratory conditions: mild steel, galvanized steel, copper, brass, nickel, Monel alloy 400, zinc and aluminum alloys. In the field tests, corrosion rates were determined for specimens subjected to alternate immersion and exposure at high tide and low tide or buried in the sea bed, for one month in each case. In the laboratory tests specimens were totally immersed in natural sea water for one month and experiments were conducted to study the influence of temperature and pH on corrosion by sea water. Mild steel samples were used to determine effect of inhibitors (potassium chromate, sodium nitrite, sodium arsenate) and of sea water velocity on corrosion rate and were also totally immersed for 24 hours in artificial sea water and in 0.1N NaCl solution. Under intermittent exposure, copper and brass had lowest corrosion rates and nickel and Monel alloy 400 suffered least corrosion when buried in sea bed. It was found in general, corrosion rate of specimens buried at half-tide level was greater than of those buried in sea bed. Rates of corrosion in laboratory tests were greater than under natural conditions and velocity, temperature and pH of test solutions are shown to have had a considerable influence on results.

119

Kirk, W. W., Covert, R. A., and May, T. P. CORROSION BEHAVIOR OF HIGH-STRENGTH STEELS IN MARINE ENVIRONMENTS. Metals. Eng. Quart., 8 :no. 4: 31-38: Nov. 1968.

The performance of 18Ni and 12Ni-5Cr-3Mo maraging steels and HY 80 and 4340 low-alloy steels in long-term corrosion tests (up to three years) is described. Cathodic protection is shown to be an effective method of minimizing corrosion and improving corrosion fatigue strength. The danger of H<sub>2</sub> embrittlement from excessive cathodic polarization of the 12Ni-5Cr-3Mo steel is discussed. The atmospheric corrosion resistance of the maraging steels was found to be greater than that of the other grades. In sea water, all specimens corroded uniformly, with the exception of 12-5-3 material, which suffered severe pitting. This pitting was eliminated by cathodic protection with mild steel anodes. Specimens of 18Ni material with yield strengths on the low side were more resistant to stress corrosion cracking than specimens of higher strength. The effect of thermal history on the cracking behavior of the maraging steels was observed. In addition to providing cathodic protection,

mild steel was particularly beneficial as a barrier coating on the maraging grades.

120

Koshelev, G. G., Rozenfel'd, I. L.  
CORROSION RESISTANCE OF LOW-CARBON AND LOW-ALLOY STEELS IN SEA WATER. Sudostroenie, 25: 12-17, November 1959.

In Russian

Steel sheet specimens (260 x 180 x 3 mm), rolled and normalized without removal of the oxide, or normalized with subsequent removal of the oxide, were mounted in steel frames, the frames placed between porcelain insulating plates to protect them from mechanical damage, and immersed in the sea at depths of 30 and 85 cm for periods up to 6 yr. Corrosion of the samples was evaluated visually and by weight loss after removal of corrosion products by cathodic polarization in 20% sodium hydroxide at a current density of 3-5 amp/sq dm.

Visual examination showed that the low-alloyed steels MS-1 and SKhL-1 corroded in a nonuniform manner, and showed more localized damage than the carbon steel ST-3 and the low-alloyed steel MK. The average corrosion rate was about the same for all steels from which the oxide layer was not removed. During 6 yr, the average weight loss was 2.5 to 3 kg/sq m, or 0.5 kg/sq m per yr. The depth of corrosion averaged 0.2 mm/yr for SKhL-1 and MS-1 steels, 0.12 mm/yr for MK steel, and 0.008 mm/yr for the carbon steel ST-3. Removal of the oxide layer after heat treatment reduced the corrosion rate of all steels by approximately 10%, and decreased the tendency of the low-alloyed steels toward localized corrosion. After 5 yr immersion in sea water the tensile and yield strengths of the steels decreased 20 to 37%, the reduction being greatest for steel SKhL-1, which also had the highest tendency toward nonuniform corrosion. The rate of mechanical strength loss was high during the first 2 yr, then levelled off. Removal of the oxide layer somewhat reduced the overall loss of mechanical strength, and resulted in a more uniform rate of loss during the 5 yr. period.

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Koshelev, G. G., Rozenfel'd, I. L.  
CORROSION STABILITY OF LOW-CARBON AND LOW-ALLOY STEELS IN SEA WATER. Foreign Tech. Div., Air Force Systems Command. Report No. FTD. TT, MT63 125, 64 71405. AD 605 881: 8 p., Dec. 1963.  
Transl. of Akademiia Nauk SSSR. Institut Fizicheskoi Khimii, Trudy, 8: p. 333-344, 1960.

122

Krafack, Karla, Franke, Erich. CORROSION BEHAVIOR OF 90/10 COPPER-NICKEL ALLOYS CONTAINING IRON. Werkstoffe u. Korrosion 4: 310-315: Aug./Sept. 1953.

In German

Sea-water-exposure tests showed that small amounts of iron improve the corrosion resistance of 70/30 copper-nickel alloys and that 90/10 copper-nickel alloys with up to 2% iron develop satisfactory corrosion resistance without quenching and annealing. Contrary to pure copper-nickel alloys, such as monel metal, those containing iron are resistant to marine growth in both quiet and flowing sea water.

After 998 days' immersion in quiet sea water, coldrolled 88/12 copper-nickel alloy sheet containing 1.81% iron showed weight loss and pitting depth only one third that of 70/30 copper-nickel alloy sheet containing no iron. Under the same conditions but over a longer period, 90/10 copper-nickel alloys were attacked only one sixth as severely as arsenic-containing admiralty brass. When exposed for 300 days to flowing sea water (0.122 m per sec), annealed 90/10 copper-nickel alloys with 0-3.5% iron content all showed good corrosion resistance. Quenched samples containing 0.8-2.2% iron were more strongly attacked than were the corresponding non-quenched compositions. The 90/10 copper-nickel alloys containing 0.7-2% iron also showed good corrosion resistance for over 41 days in sea water at velocities up to 3.658 m per sec. They were superior to admiralty brass and to low-iron 70/30 copper-nickel alloys, and equivalent or superior to aluminum brass and high-iron 70/30 copper-nickel. Similar tests on 70/30 copper-nickel alloys showed that pitting decreases as the iron content increases. Quench annealing has no effect on 1.5% iron alloy, but is beneficial for the 2.0% iron alloy and mandatory for the 3.5% iron alloy.

Corrosion-erosion tests on disks rotated in sea water at various velocities for 55 days at 0.6 C showed that corrosion resistance is 1% lower in samples heat-treated to precipitate the iron-rich phase and that 90/10 alloys are better than 70/30 copper-nickel alloys.

Exposures of condenser pipes, internally protected by a 2.1 lead-tin coating, to water flowing at 3 m and even at 4.57 m per sed at 9-16 C for up to 10 mo again demonstrated the remarkable corrosion resistance of 70/30 copper-nickel alloys

containing 0.52% iron and particularly of 90/10 alloy pipes containing 1.5-2% iron. Welds in 70/30 copper-nickel alloys with or without 0.5% iron performed well in service over a period of 2 yr.

Galvanic corrosion tests showed that the 90/10 alloy is more easily polarized in turbulent sea water than is pure copper, but that copper can be replaced by 90/10 copper-nickel in contact with a less noble metal such as cast iron without disadvantage. The 70/30 copper-nickel alloy is much more susceptible to galvanic corrosion than is the 90/10 alloy.

The 90/10 copper-nickel alloys retain their corrosion resistance at elevated temperatures, say 163 C, for 54 days. Spray tests at 49 C revealed that an iron content of 1% produces the most favorable results. Pipes of 90/10 copper-nickel with 0.7% iron lasted more than 4 yr in sea water, whereas admiralty brass pipes showed considerable corrosion after 1-2 yr. Copper-nickel alloys 90/10 with up to 1.5% iron also showed satisfactory results.

Chlorination of salt water produced no substantial change in the corrosion behavior of 90/10 copper-nickel alloy. Corrosion resistance decreased, however, with rising iron content. Best results in the 70/30 series were obtained with 0.4% iron content.

The 70/30 alloy is more resistant to attack by hydrogen sulfide, ammonium hydroxide, and hydrochloric acid than the 90/10 alloy. Welded and soldered 90/10 copper-nickel pipe showed satisfactory resistance to sea-water corrosion.

123

Kubose, D. A., Cordova, H. I. ELECTRO-CHEMICAL CORROSION STUDIES OF SNAP CONTAINER MATERIALS. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-1036, AD-635 682; Contract AT(49-S)-2084: 28 p., June 1966.

Corrosion rates of Haynes 25, Hastelloy C and Hastelloy N in natural seawater were determined by galvanostatic polarization techniques. Values of approximately 0.01 mils per year were obtained for each of the alloys. No significant effect of aeration and solution stirring on the corrosion rates was observed.

124

Kubose, D. A., Lai, M. G., Goya, H. A., Cordova, H. I. MEASUREMENT OF SEAWATER CORROSION OF SNAP CONTAINER ALLOYS USING RADIOACTIVE TRACER TECHNIQUES. Naval Radiological Defense Laboratory. Report

No. USNRDL-TR-1092, AD-645 553: 45 p., January 1967.

Corrosion rates of Haynes 25, Hastelloy C and Hastelloy N in seawater were measured using two radioactive tracer techniques. These techniques involved (1) measurement of the radioactivity leached into seawater from radioactive alloy specimens and (2) performing neutron activation analysis of corrosion products in seawater in which inactive alloy specimens had been placed. The second technique was used to determine whether the gamma recoil from the thermal neutron activation of the alloys in the first technique had affected their corrosion properties. It was found that the gamma recoil from neutron activation had only a small effect on the corrosion rate of the alloys. The average corrosion rates obtained for hastelloy C and Hastelloy N were 0.00005 mil per year and 0.0001 mil per year, respectively. No appreciable differential leaching of the cobalt, nickel and chromium components of these alloys was observed. The results obtained for Haynes 25 indicated differential leaching had occurred. The corrosion rate calculated from the amount of cobalt released was 0.000001 mil per year while that calculated from the amount of chromium released was 0.00001 mil per year.

125

Kubose, D. A., Cordova, H. I. CORROSION STUDIES OF HAYNES 25 ALLOY IN SEAWATER USING ELECTROCHEMICAL TECHNIQUES. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-67-64, AD-656 897; Contract AT (49-5)-2084: 31 p., Aug. 1967.

Electrochemical corrosion rate measurements were made on uncoated, emissively coated and thermally shocked and uncoated specimens of Haynes 25 alloy in seawater at room temperature and 90C. The corrosion rates of the emissively coated specimens were about an order of magnitude higher than those of the uncoated specimens. No significant difference between the corrosion rates measured at room temperature and at 90C was observed for either the uncoated or the emissively coated specimens. Thermal shocking of uncoated specimens (by quenching from 500C to room temperature) did not increase their corrosion rates. The corrosion rates observed were on the order of 0.003 mils per year (MPY) for the uncoated and the thermally shocked uncoated specimens and 0.04 MPY for the emissively coated specimens.

126

Kubose, D. A., Goya, H. A., Lai, M. G.

Cordova, H. I. SEAWATER CORROSION STUDIES OF EMISSIVELY-COATED HAYNES 25: RADIO-ACTIVE TRACER TECHNIQUES. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-67-109, AD-659 978: Contract No. AT(49-5)-2084: 28 p., October 1967.

Corrosion rates of uncoated, half- and completely-emissively-coated Haynes 25 have been measured in seawater by use of radioactive tracer techniques. The corrosion rates observed for the (1) uncoated and (2) half- and completely-coated specimens were nominally 0.000003 and 0.0001 mil per year (MPY), respectively. It was established that the observed corrosion rates of the half- and completely-coated specimens were due entirely to corrosion of Haynes 25 and not to the corrosion of the emissive coating. The higher corrosion rates were attributed primarily to the fact that the actual surface area of the Haynes 25 was much larger than the geometric surface area because of surface preparation prior to application of the emissive coating. A re-examination of the corrosion rate based upon the amounts of cobalt and chromium released to the seawater indicated that the previously reported differential leaching of these components of Haynes 25 was an experimental artifact due to errors in counting extremely low amounts of chromium-51. Present observations show that the cobalt-and-chromium-based corrosion rates are the same and agree with the previous cobalt-based corrosion rate.

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Kubose, D. A., Cordova, H. I. ELECTROCHEMICAL CORROSION STUDIES OF GALVANICALLY COUPLED SNAP-21 MATERIALS. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-68-26, AD-668 161: 36 p., January 1968.

Electrochemical corrosion rate measurements on materials used in the Snap-21 radioisotopically-fueled power system have been made in seawater at room temperature. The materials examined included aluminum, copper, Hastelloy C, Hastelloy X, nickel, 3-4 stainless steel, tantalum, titanium-621 alloy and uranium-8% molybdenum alloy. The normal corrosion rate of each material was measured by means of galvanostic polarization techniques. A galvanic series of the materials in seawater was determined and the galvanic currents between galvanically coupled materials were measured with a zero-resistance ammeter circuit. The effect of galvanic coupling of construction materials of the SNAP-21 system does not materially change the containment time of the Sr-90 fuel in the corrosive seawater environment.

128

Kubose, D. A., Lai, M. G., Goya, H. A., Cordova, H. I. SEAWATER CORROSION STUDIES OF SNAP-21 MATERIALS. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-68-109, AD-678 455: Contract AT(49-5)-3002: 43 p., Dec. 1968.

The corrosion rates of several SNAP-21 materials measured in seawater at ambient room temperature and pressure (Hastelloy C, Hastelloy X, titanium-621, beryllco-165) have been compared to those measured in 200C seawater vapor (Hastelloy C, Hastelloy X), in seawater under a hydrostatic pressure of 7000 PSI (Hastelloy C, titanium-621, beryllco-165) (23C) and in seawater in an ionizing radiation field of 200,000 R/HR (Hastelloy C, Hastelloy X) (30C). Significant increases in corrosion rate were observed only for Hastelloy C and Hastelloy X in hot seawater vapor (approximately two orders of magnitude) and for Hastelloy C in seawater under high hydrostatic pressure (approximately an order of magnitude).

129

Kubose, D. A., Cordova, H. I. ELECTRO-CHEMICAL CORROSION-RATE MEASUREMENT OF GALVANICALLY COUPLED SNAP-23 MATERIALS IN SEAWATER. Naval Radiological Defense Laboratory. Report No. USNRDL-TR-69-14, AD-852 974L: 36 p., January 1969.

130

Kubota, Hiroyuki, SEA-WATER CORROSION AND STEELS RESISTANT TO IT. Nippon Kokan Tech. Rep. (Overseas), No. 10: 27-40, March 1970.

The factors affecting the corrosivity of sea water are discussed and the mechanism of marine corrosion on steel is described. Factors mentioned include salinity, flow rate, and temp. Methods of preventing corrosion by using sea-water-resistant steels are described and the development of corrosion resistant steels, e.g. 'NK Marine', 'Mariner', NEP-TEN 50 and 60, and APS 20A grades, is mentioned. The chemical compositions and mechanical properties of these steels are given and trials carried out during the development of corrosion resistant steels are reported.

131

Lagutina, A. G., Danil'chenko, K. P., Shevchenko, O. F., Barannik, V. P. THE CORROSION OF SHIPBUILDING MATERIALS IN SEA WATER. Zashchita Metallov, 6; No. 1: 48-51, 1970.

In Russian

A comparative study was made in natural

and in laboratory conditions of the corrosion in sea water of the most commonly used shipbuilding materials, i.e. (i) steel 3S [C 0.12-0.20%], (ii) bronze AMTs-9-2 [9:2 Al-Ni], (iii) monel NMZhMTs [28: 2.5: 1.6 Cu-Fe-Mn, Ni remainder], (iv) AMG-6T [Al-6% Mg contg. Ti], stainless steels (v) 1Kh18N10T [18: 10 Cr-Ni, Ti-stabilized] and (vi) OKh17N7Yu [17:7:1 Cr-Ni-Al], and (vii) brass L62 (Muntz metal, 62% Cu). Specimens were immersed 40 m from the shore at various depths and in the laboratory in flowing and stagnant sea water. Corrosion rates were higher in natural conditions than in laboratory tests (artificial or natural sea water), e.g. after 1 year the corrosion rates of (ii), (vii) and (iv) were 5-6 times higher in the sea. With (iii), (v), and (vi) there was also a difference in the type of corrosion severe pitting in the sea but very little attack in the laboratory. With (i) rates were similar in the sea and laboratory flowing sea water tests but lower in stagnant tests. The principal factors responsible for the increased attack in natural conditions were biological (affecting the physicochemical properties of the sea water) and mechanical (natural movement affecting the cathodic process).

132

Langer, N. A., Ryabov, V. P., Zotova, L. M. NATURAL CORROSION STUDIES OF ALUMINUM-STEEL WELDED JOINTS. *Avtom. Svarka*, 21: No. 4; 23-28, April 1968.

In Russian

The corrosion resistance of joints of AMts and AMg6 to St.3 and Kh18N10T in sea-water and in air near the sea was studied. Specimens were exposed to sea atmospheres 10d- 12 months. After 8 months, AMg6/kh18N10T joints had the highest corrosion resistance. Mechanical properties of joints are tabulated.

133

Laque, F. L. SEA WATER CORROSION TESTS. In: *Corrosion Handbook*, Herbert Uhlig, ed. New York, Wiley, p. 1060-1071, 1948.

134

Laque, F. L. BEHAVIOR OF METALS AND ALLOYS IN SEA WATER. In: *Corrosion Handbook*, Herbert Uhlig, ed. New York, Wiley, p. 383-430, 1948.

135

Laque, F. L. A CRITICAL LOOK AT SALT SPRAY TESTS. *Materials & Methods*, 35: No. 2: 77-81, February 1952.

The author appraises the value of salt-spray tests and concludes that they are inadequate. They should not be used as a guide in research and should not be substituted for special tests designed to study, individually or in combination, those factors which determine the overall quality of products to be improved. A salt-spray test can be useful for inspecting different modifications of the same kind of metal. It can also be used for different lots of the same product once some standard level of performance has been established; however, success or failure in the test does not guarantee similar behavior in actual service.

Specific criticisms directed at the test are as follows: There is rarely a parallel between conditions in the salt-spray box and those prevailing in nature. Consequently the assumption that exposure to salt spray for several hours is equivalent to natural exposure for months or years is not warranted. Moreover, the mode or pattern of deterioration produced does not match that observed in service. Accurate measurements of the protective value of either metal or nonmetal coatings are not possible.

With nonmetal coatings, the test is not reliable because the environment of the salt-spray test is designed to be destructive to the base metal rather than to the coating, and assessment of coating behavior is based on corrosion of the metal base rather than the coating. The effects of light and moisture on lacquers and enamel coatings or the effects of wind-driven rain or intense sunlight on protective oil and grease coatings cannot be duplicated. Accurate determination of discontinuities in a protective coating is hampered by formation of new discontinuities if the test is run too long or by differences in the amount of fog condensing on surface portions that are exposed at different angles. The effect of slope and angle of exposure also prevents the test from being valuable as a measure of coating thickness.

Galvanic effects cannot be accurately observed because conditions within the salt-spray box cannot be made to duplicate those existing in other corrosive media. The accumulation of soluble corrosion products exaggerates their secondary corrosive effects. Galvanic action is also influenced by the relatively high electrical conductivity of films of condensed brine as compared with films of condensate that form on metal surfaces in natural environments. This tends to increase the areas

involved in galvanic couples with an increase in galvanic action.

The test is also unreliable for the detection of free iron which contaminates the surface of stainless steel.

136

LaQue, F. L. THEORETICAL STUDIES AND LABORATORY TECHNIQUES IN SEA WATER CORROSION TESTING EVALUATION. Corrosion, 13: 303t-314t, 1957.

137

LaQue, F. L., Tuthill, A. H. ECONOMIC CONSIDERATIONS IN THE SELECTION OF MATERIAL FOR MARINE APPLICATIONS. Society of Naval Architects and Marine Engineers. Transactions 69: 1-21, 1962.

138

LaQue, F. L., and Copson, H. R. eds. CORROSION RESISTANCE OF METALS AND ALLOYS, 2nd. Edition. New York, Reinhold, p. 332., 1963.

139

LaQue, F. L. PRECAUTIONS IN INTERPRETATION OF CORROSION TESTS IN MARINE ENVIRONMENTS. Industrie Chimique Belge, Brussels, 29: No. 11: 1177-1185, Nov. 1964.

140

LaQue, F. L. MATERIALS SELECTION FOR OCEAN ENGINEERING. In: Ocean Engineering, Wiley and Sons, Inc., New York. p. 588-632, July 1968.

This review of the requirements of materials for use in ocean engineering applications will concentrate on resistance to deterioration in ocean environments. This is justified by the fact that such requirements represent the principal distinction between ocean-engineering and other engineering applications. The usual properties related to the strength of structures and devices and how they may be fabricated are not peculiar to ocean-engineering applications and can be dealt with by reference to voluminous pertinent literature, much of it recently related to projected designs for pressure vessels, etc., proposed for undersea use.

141

LaQue, F. L. DETERIORATION OF METALS IN AN OCEAN ENVIRONMENT. In: Proceedings, International Symposium, Held in New York City, Sept. 12-14, 1967. Ocean Engineering, 1: No. 2: 121-199, Dec. 1968 and 1: No. 3; 299-314, Feb. 1969.

Discussion is concentrated on the types of deterioration and the circumstances under which it occurs for the several classes of material employed in ocean

engineering applications. Suggestions as to how difficulties may be avoided are given equal attention. Aluminium alloys are dealt with in terms of alloy selection, effects of deep submergence, stress corrosion, effects of high temperatures and galvanic action. The copper base alloys are discussed in terms of tolerance for velocity effects, sulphide pollution, stress-corrosion, and such selective attack as dezincification, etc. The stainless steels and nickel base alloys are considered with respect to susceptibility to pitting, crevice corrosion, and stress-corrosion. Titanium and the superstrength steels are discussed principally with respect to resistance to stress-corrosion cracking (SCC). Galvanic action and cavitation erosion phenomena are dealt with generally in terms of all classes of material.

142

LaQue, F. L. ANALYSIS OF MARINE CORROSION FAILURES. In: Failure Analysis, 1969, 299-320, 322-326. Met. A., 6907-72 0113.

Analysis of marine corrosion failures is described in terms of the many factors that must be considered, in three broad categories. These categories cover factors related to the metal, to the environment and to design. This approach is illustrated by case histories devoted to instances in which certain factors were of dominant importance. These included an inadequate content of a critical element, dezincification, stress effects, graphitization, too high a velocity, uneven velocity, crevice corrosion, vibration, cavitation, cyclic stresses, micro- and macro-organisms, stray currents, galvanic effects and metal salts. Examples of accelerated corrosion include the effect of Cu corrosion products on Al in a heat exchanger assembly and the attack of Al or Ni-Cu tubing by Hg leached from antifouling paints. Cavitation erosion of Mn bronze marine propeller blades is discussed.

143

Larrabee, C. P. CORROSION OF STEELS IN MARINE ATMOSPHERES AND IN SEA WATER. Carnegie-Illinois Steel Corp., Corrosion Research Laboratory. Trans. Electrochem. Soc. 87: 123-140, 1945.

In sea water, plain and low-alloy steels are shown to have an average corrosion rate of about 22 mg/dm<sup>2</sup>/day (0.004 in./yr average penetration). Pitting attack characterizes the corrosion of stainless steels, although the presence of 2 - 3% molybdenum in 18/8 stainless or very high alloy content diminishes this tendency.

144

Larrabee, C. P. CORROSION RESISTANCE OF HIGH-STRENGTH, LOW-ALLOY STEELS AS INFLUENCED BY COMPOSITION AND ENVIRONMENT. Corrosion, 9: No. 8: 259-271, Aug. 1953.

145

Larrabee, C. P. CORROSION-RESISTANT EXPERIMENTAL STEELS FOR MARINE APPLICATIONS. Corrosion, 14: No. 11: 501t-504t, 1958.

146

Larrabee, C. P. STEEL HAS LOW CORROSION RATE DURING LONG SEA WATER EXPOSURE. Materials Protection, 1: p. 95-96, December 1962.

Twenty H-sections of carbon steel piles immersed 23.6 yr in unpolluted sea water at Santa Barbara, Calif., cleaned in the field and measured (at 3 in. from each of the four edges), showed an average annual flange loss of  $1.53 \pm 0.23$  mils. End sections of nine piles cleaned and measured in the laboratory had average annual losses of: flanges, 1.34 mils; webs, 1.72 mils; weighed average,  $1.46 \pm 0.25$  mils. Annual weight losses of the nine end sections averaged  $1.73 \pm 0.21$  mils. After 20 yr, an annual loss of 1 mil is predicted.

147

Lee, R. W. H. BIBLIOGRAPHY ON MICROBIAL CORROSION OF METALS. Prevention of Deterioration Center, National Academy of Science, National Research Council. Report No. S63 025, PDL48074, AD-601 247: 74 p., July 1963.

148

Lennox, T. J., Jr., Peterson, M. H., Brown, B. F., Groover, R. E., Newbegin, R. L., Smith, J. A., Waldron, L. J. MARINE CORROSION STUDIES, STRESS CORROSION CRACKING, DEEP OCEAN TECHNOLOGY, CATHODIC PROTECTION, CORROSION FATIGUE; FOURTH INTERIM REPORT OF PROGRESS. Naval Research Laboratory, Memorandum Report No. 1711, 127 pgs., May 1966.

This is the Fourth Interim Report of Progress made in Marine Corrosion Studies conducted by the METALLURGY DIVISION OF NRL. It provides information on studies which are underway. Conclusions reached are preliminary in nature. These deal with four experimental areas: stress-corrosion studies, cathodic protection studies, metallic corrosion studies, and corrosion fatigue studies. Marine corrosion research is characterized at the present time by the necessity to conduct experiments that often may extend over a period of many months or even years. In some instances the intermediate evaluations may provide the only available guidance at the time in a given problem area.

149

Lennox, T. J., Jr., Peterson, M. H., Groover, R. E. MARINE CORROSION STUDIES: THE ELECTROCHEMICAL CHARACTERISTICS OF SEVERAL PROPRIETARY ALUMINUM GALVANIC-ANODE MATERIALS IN SEA WATER (FIFTH INTERIM REPORT OF PROGRESS). Naval Research Laboratory. Memorandum Report No. 1792, 40 p., May 1967.

150

Lennox, T. J., Jr., Peterson, M. H., Groover, R. E. MARINE CORROSION STUDIES: THE CORROSION CHARACTERISTICS AND RESPONSE TO CATHODIC PROTECTION OF SEVERAL STAINLESS STEEL ALLOYS IN QUIESCENT SEA WATER; WITH A PARTIALLY ANNOTATED BIBLIOGRAPHY. Naval Research Laboratory, Memorandum Report No. 1948, AD-684 073: 52 p., Nov. 1968.

Crevice corrosion was the most serious type of attack found on unprotected stainless steel, but random pitting not associated with any observed crevice was also found. Stainless steel alloys 21CR-6NI-9MN, 17-4 PH H1025, 205, 304, 316, 410, and 430 were seriously attacked by crevice corrosion. Stainless No. 20CB-3 was much more resistant to this type of attack but was not completely immune. Cathodic protection from either carbon steel or aluminum anodes effectively reduced the crevice corrosion on the stainless steels studied, but in some cases the steel anodes were not effective in reducing the depth or incidence of random pitting. Aluminum anodes are judged unsuitable for use on 17-4 PH H1025 stainless steel as this level of cathodic protection caused accelerated cracking of this alloy. Additional studies on cathodically polarized 17-4 PH stainless steel (aged at 925F for 4 hours) indicated a considerable reduction in the load-bearing capacity of a precracked specimen when it was polarized to the potential of a zinc or aluminum anode.

151

Lennox, T. J. Jr., CORROSION ANALYSIS OF 304 STAINLESS STEEL WIRE ROPE AND FITTINGS FROM A NOMAD BUOY MOORING SYSTEM AFTER 34-MONTHS CONTINUOUS SERVICE IN THE GULF OF MEXICO. Naval Research Laboratory. Memorandum Report No. 2045, 20 pgs., Sept. 1969.

Samples for a 1250-ft length of 304 stainless steel wire rope and associated stainless steel tube thimbles and stainless steel cable clamps were studied to determine the extent of corrosion after 34-months continuous immersion in the Gulf of Mexico. This 3/4-in.-diam wire rope (6 x 19 Warrington - IWRC 7 x 7) was used in the upper portion of a Nomad buoy mooring system. The performance of this particular buoy

design is important because of its possible influence on the national buoy program.

152

Lennox, T. J., Groover, R. E., Peterson, M.H. CORROSION AND CATHODIC PROTECTION OF WIRE ROPES IN SEAWATER. In: Sixth Marine Technology Society Conference, Corrosion Symposium, Wash. D. C., 29 June - 1 July, 1970. Marine Technology Society, Vol. 2: p. 1281-1294, 1970.

153

Lindberg, R. I., ALUMINUM IN MARINE ENVIRONMENTS. Am. Soc. Naval Engrs. J., 73: 133-138, February, 1961.

154

Little, Arthur D. Inc. MARINE CORROSION AND FOULING. Report, Proj. Trident, AD-415 256: 32 p., n.d.

The nature, causes, and prevention of marine corrosion and fouling are reviewed. Emphasis is given to those anticipated Trident problems which lie outside the more familiar corrosion and fouling experience. In particular, an effort is made to determine to what extent coastal waters test data, and service data from from ships, buoys, and cables may be applied to other environments and devices. The electrochemical mechanism of corrosion is discussed as a framework for understanding the effects of the various factors which influence corrosion rate: for example, temperature, oxygen concentration acidity, bimetallic coupling, organic excretions, and protective coatings. Mention is made of such special problems as pitting, stress corrosion cracking, and interaction of fouling with corrosion. Marine fouling, together with the destructive effects of marine borers on woods and plastics, varies widely and often unpredictably with geographical location, temperature, water velocity, depth and a host of other factors, current knowledge of corrosion and fouling effects are summarized.

155

Loginow, A. W. CORROSION OF EXPERIMENTAL SUBMARINE HULL STEELS IN MARINE ENVIRONMENTS. United States Steel Corp. Applied Research Lab. Report No. S-13305, and S-23309-1, AD-482 784L: Contract Nobs-88540. 21 p., September 1965.

156

Loginow, A. W. CORROSION OF 12NI-5CR-3MO MARAGING STEEL WELDMENTS. United States Steel Corp., Applied Research Lab. Tech. Report No. ARL-B-63502, AD-817 367L: Contract, Nobs-94535, 27 p., July 1967.

157

Loginow, A. W. FOUR-YEAR CORROSION TESTS OF HY-130 AND HY-80 STEELS IN MARINE ENVIRONMENTS. United States Steel Corp., Applied Research Lab. Tech. Report, AD-855 821L: Contract Nobs 94535. 25 p., July 1969.

158

Loginow, A. W. FOUR-YEAR CORROSION TESTS OF 12NI-5CR-3MO MARAGING STEEL IN MARINE ENVIRONMENTS. Tech. Report, AD-855 822L: 22 p., July 1969.

159

Lowe, T. A. INVESTIGATION OF THE CORROSION RESISTANCE OF ALUMINUM-STEEL ASSEMBLIES EXPOSED TO SEA WATER. PART I: ASSEMBLY FABRICATION AND INSTALLATION. Kaiser Aluminum and Chemical Corp. Report No. MS PR61 67, AD-440 865L: Contract Nobs 72433. 14 p., September 1961.

160

Lowe, T. A. INVESTIGATION OF THE CORROSION RESISTANCE OF ALUMINUM-STEEL ASSEMBLIES EXPOSED TO SEA WATER. PART II. FIRST VISUAL INSPECTION. Kaiser Aluminum and Chemical Corp., Report No. MS PR62 64, Interim Progress Rept. No. 20, AD-441 658L: Contract Nobs 72433. 4 p., Nov. 1962.

161

Lowe, T. A. INVESTIGATION OF THE CORROSION RESISTANCE OF ALUMINUM-STEEL ASSEMBLIES EXPOSED TO SEA WATER. PART III: EVALUATION OF ONE-YEAR SAMPLES. Kaiser Aluminum and Chemical Corp. Report No. MS PR63 10, Progress Report No. 21, AD-431 266: Contract Nobs 72433. 35 p., March 1963.

The first set of riveted, aluminum-steel assemblies was removed after exposure in tide-range immersion for one year. An evaluation of these assemblies was made on the basis of exterior appearance, the condition of faying surfaces, and a comparison of their breaking strength with unexposed, control samples. The results of this evaluation show that (1) there has been a small loss in the breaking strength of exposed assemblies, (2) the attack of faying surfaces is more a function of the protective paint and joint insulation system than of the rivet material or the aluminum alloy used in the assembly, and (3) significant attack of aluminum exterior surfaces by copper, deposited from the anti-fouling paint used, may cause significant damage of the samples still in test before completion of the program.

162

Lowe, T. A. INVESTIGATION OF THE CORROSION RESISTANCE OF ALUMINUM-STEEL ASSEMBLIES

EXPOSED TO SEAWATER. PART IX: EVALUATION OF FIVE-YEAR SAMPLES. Kaiser Aluminum and Chemical Corp. Report No. MS-PR-66-43, Progress Rept. No. 27, AD-484 896L: Contract No. NObs-72433. 54 p., May 1966.

163

Macander, Aleksander, Francy, C. D. INSTALLATION OF NASL DEEP SEA MATERIALS EXPOSURE ARRAYS IN THE TONGUE OF THE OCEAN. Naval Applied Science Lab. Report No. NASL-930-6, Progress Rept. No. 1, AD-818 426L: 25 p., July 1967.

164

Maersch, R. E. THE EFFECT OF MINOR ALLOYING ADDITIONS ON THE SEA-WATER CORROSION BEHAVIOR OF ALUMINUM-BRONZE ALLOYS. U.S. Navy Marine Engineering Laboratory, Report No. MEL 196/66, AD-635 288: 18 p., June 1966.

Some compositions of aluminum-bronze alloys suffer an insidious type of selective-phase attack in seawater. One proposed method to improve the corrosion behavior of these materials was the addition of minor alloying elements to promote the formation of microstructural constituents that are electrochemically compatible. Three experimental alloys, containing small amounts of tin, nickel and arsenic, respectively, were analyzed after sea-water exposure. None of the minor alloying additions imparted significant improvement in corrosion behavior of the base alloy.

165

Mafflard, J. AN EXAMPLE (AMONG OTHERS) OF THE EXCELLENT CORROSION RESISTANCE OF ALUMINIUM ALLOYS IN SEA-WATER: 20 YEARS IMMERSION WITHOUT A TRACE OF CORROSION. Revue Aluminium, No. 386: 638, June 1970.

In French

A mooring buoy which has been in service since 1950 is illustrated. Fabricated in 3-mm Duralinox A-G5, the buoy shows no sign of corrosion. It has been taken from the water only three times in 20 years for attention to the chain and securing rings. This is one of numerous examples of the good resistance of Al alloys to marine conditions.

166

May, T. P., Weldon, B. A. COPPER-NICKEL ALLOYS FOR SERVICE IN SEA WATER. In: Proceedings, Congres International de la Corrosion Marine et des Salissures, Cannes, France, June 8-12, 1964. p. 141-156, 1965.

167

McGoff, V. M. J., Glaser, C. J. CORROSION OF INCONEL BY SEA WATER. MSA Research Corp. Progress Report MSA Memo. 138, Contract No. NObs 77023: 15 p., Jan. 20, 1959.

168

Mears, R. B. and Brown, R. H. RESISTANCE OF ALUMINUM-BASE ALLOYS TO MARINE EXPOSURES. Trans. Soc. Naval Architects Marine Engrs. 52: 91-113, 1944.

In order to study corrosion in various alloys, the Aluminum Research Laboratories have tested over 100,000 specimens. The compositions and properties of the aluminum alloys examined are given. In most tests, the comparative resistance to corrosion was evaluated by the change in mechanical properties after various periods of exposure. In addition, the exposed samples were often sectioned and the depth and type of attack determined by microscopic examination.

Alloy specimens were exposed in a variety of sea and harbor waters. Generally, 1 set of specimens was exposed continuously submerged in the water and another was placed at tide level where it was alternately immersed in water and exposed to air. Periods of exposure were 1 and 2 yr. for each sample, depending upon the test site. Results indicate that all the aluminum alloys tabulated have a high resistance to sea water. Alclad 3S and Alclad 24S-T are the most resistant alloys; neither showed significant changes in tensile strength at any location. Alloy 52S-1/2H is the next most resistant, followed by 52S. Alloys 53S-T and 61S-T are similar and somewhat inferior to 52S. Aluminum-copper alloys, such as 17S-T and 24S-T, are definitely attacked in sea water and should not be used in such locations unless protected.

Galvanic effects caused by contact between dissimilar metals are likely to be more pronounced in marine exposures than in many other locations because of the high conductivity of the sea water. Aluminum alloys are anodic to most of the other common structural alloys. A potential series for the common aluminum alloys and other materials is included in the report. Metals high in this series tend to corrode selectively and protect metals lower in the series.

Contact of either magnesium or zinc with aluminum alloys in sea water will result in an increased attack of the magnesium or the zinc. In the case of the magnesium-

aluminum alloy couple, sufficient current may flow to the aluminum alloy to cause special cathodic corrosion. Magnesium-base alloys are the only structural base alloys which have been found to cause this special cathodic corrosion. Aluminum-base alloys containing substantial amounts of magnesium are resistant to cathodic corrosion of this type.

Contact between aluminum alloys and unalloyed and stainless steels normally results in some selective attack of the aluminum alloy.

Contact between aluminum alloys and copper generally leads to very pronounced selective attack of the aluminum alloy. Copper alloys such as brass or bronze or nickel alloys such as cupro-nickel or monel behave like copper itself when in contact with aluminum alloys.

If aluminum alloys must be employed with copper or copper alloys in structures immersed in sea water, the use of zinc attachments for cathodic protection is one of the most satisfactory measures. The zinc will be selectively attacked, and the electric current generated will protect both aluminum and copper.

169

Mendizza, A. THE STANDARD SALT-SPRAY TEST: IS IT A VALID ACCEPTANCE TEST? Am. Soc. Testing Materials. Spec. Tech. Publ. 197: p. 107-126, 1957.

Comparative salt spray tests were run on nickel plated NAX or 1010 steel. Plate thicknesses were 0.00075 to 0.0015 in., 0.0015 in. over copper flashing, and 0.006 in. over 0.009 in. copper. All specimens received a final 0.00002 in. thick coating of chromium. Sets of sixteen replicate panels were distributed among four laboratories and tested in four separate runs in accordance with ASTM Method B-117 (20% salt solution). Rust spot counts were made after every 24 hr period. Total test time varied from 48 to 96 hr depending on plate thickness.

A statistical analysis of results from three of the coating systems showed that the test boxes were not consistent nor were the platers. Although data are given as both large and small rust spots, these measures were not statistically independent and the test laboratories showed a strong negative correlation between small spots and large spots. The platers, on the other hand, show a strong positive correlation between size of spots. In all three cases, the residual variation, i.e., the factor which statistically is over and

above variations attributed to plater and tester, was quite large, and would require sample sizes of about 10 sq ft in order to determine specification requirements of not more than six rust spots per sq ft of area. It was concluded that the salt spray test procedure as currently practiced fails to perform as a standard test.

170

Metals and Controls Inc. EVALUATE, TEST AND MANUFACTURE AN IMPROVED WIRE ROPE AND CABLE. Quarterly Progress Rept. No. 6, AD-807 266: Contract No. NObS-92232. 23 p., September 2, 1966.

The data resulting from post-exposure testing after six-months in seawater are presented showing general and specific corrosion of the various materials tested. Post-exposure and pre-exposure tensile test data are presented for comparison and the only material that exhibited a significant strength loss was solid stainless steel in the 5,000 pound and 10,000 pound mooring tests.

171

Milligan, S. SAMPLE TEST EXPOSURES TO EXAMINE CORROSION AND FOULING EFFECTS ON MATERIALS IN THE DEEP OCEAN. Naval Underwater Ordnance Station. Report No. TM-359, AD-477 273: 44 p., January 1966.

172

Moeller, Richard. SEA WATER CORROSION OF ENGINEERING MATERIALS. Undersea Technology, 4: p. 20-23, April 1963.

173

Munitz, A. J. ANALYZING FAILURES OF OCEAN COMMUNICATIONS CABLE. Undersea Technology, 7: No. 5: 45, 47-49, May 1966.

174

Muraoka, J. S. THE EFFECTS OF MARINE ORGANISMS ON ENGINEERING MATERIALS FOR DEEP-OCEAN USE. Naval Civil Engineering Lab., Report No. R-182, AD-287 952: March 1962.

A literature survey was made of the effects of Marine organisms on various types of engineering materials particularly in deep-ocean environments. Numerous materials such as manila ropes, cotton fishing nets, petroleum hydrocarbons, rubber products, steel, submarine cables (telegraph and telephone), concrete, and cork (floats) have been attacked and destroyed by various marine organisms in various depths, from shallow protected waters to ocean depths exceeding 7,200 feet. Marine organisms which have been observed to be responsible for the destruc-

tion of these materials include species of wood- and rock-burrowing animals, purple sea urchins, sharks, fish and microorganisms.

A proposed field and laboratory study to accumulate further biological and engineering data about the relative behaviors of various materials to marine biological deterioration is presented.

175

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS. PART I. FOUR MONTHS AT 5,640 FEET. Naval Civil Engineering Lab. Report No. NCEL-TR-329, AD-608 939: 39 p., November 1964.

This is part I of a series of reports on the biodeterioration of materials in the deep ocean. It covers the data obtained by sampling mud, sea water, and rocks, and data obtained by exposing 1,324 specimens of 492 materials for 4 months on the Pacific Ocean floor at a depth of 5,640 feet. The materials were attached to a submersible test unit (STU). The STU was retrieved in February 1964, and returned to the Laboratory for tests and analyses. There were no marine fouling organisms attached to the metal test specimens. Some of the plastic materials were covered with a bacterial slime growth. Cotton rope, manilla hemp rope, and burlap wrappings were deteriorated by microbial activity. Pine test panels and manila hemp rope were attacked by marine boring organisms (*Xylophaga Washingtona* Bartsch). Various species of fouling organisms were found on rock samples collected from the ocean floor in the vicinity of the STU test site. Also presented are equipment and methods for obtaining samples and data on oceanographic cruises as well as those used with the STU.

176

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS, PART II. SIX MONTHS AT 2,340 FEET. Naval Civil Engineering Lab. Report No. NCEL-TR-393, AD-619 014: 48 p., August 1965.

This is part II. of a series of reports on the biological deterioration of materials in the deep ocean. It covers the data obtained after exposing 2,385 specimens of 603 different materials for 6 months (197 days) on the Pacific Ocean floor at a depth of 2,340 feet (Test site II.). The materials were attached to a submersible test unit (STU). The STU was retrieved in December 1964 and returned to the Laboratory for test and analysis. There were marine fouling organisms attached to the plastic ropes, aluminum buoys, polyethylene-jacketed wire rope,

nickel-plated shackles, and on some metal test specimens. Most of the plastic and all of the rope materials were covered with bacterial slime growth. Wood panels, plastics, and manila rope were attacked by marine borers. Cotton and manila rope specimens and jute-fiber burlap wrappings were severely deteriorated by bacterial action. Metal, glass, natural and butyl rubber, and some plastics with a smooth and extra hard surface were not affected. The biological effects on materials recovered from test site II are briefly compared with materials recovered from test site I.

177

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS. PART III. THREE YEARS AT 5,300 FEET. Naval Civil Engineering Lab. Report No. NCEL-TR-428, AD-631 078: 53 p., February 1966.

The report covers data obtained after exposing 1,318 test specimens of 316 different materials for 35 months on the Pacific Ocean floor at a depth of 5,300 feet. The materials were attached to a submersible test unit (STU). The STU was retrieved in February 1965 and returned to the Laboratory for tests and analyses. Hydroid growths were found on all the test specimens placed on the STU. A few species of tube worms were found attached to metals, plastics, and coated test specimens. Most of the plastics and all the rope materials were covered with bacterial slime growth. Cotton and manila rope specimens were severely deteriorated by bacterial action. Wood panels, plastics, and manila ropes were attacked by marine borers, metals, natural and butyl rubber, and certain plastic materials were not affected.

178

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS, PART IV. ONE YEAR AT 6,800 FEET. Naval Civil Engineering Lab. Report No. R-456, AD-636 412: June 1966.

As Part IV of a series of reports on the biological deterioration of materials in the deep ocean, this report covers the data obtained after exposing metallic and nonmetallic specimens for 13 months on the floor of the Pacific Ocean at a depth of 6,800 feet (test site I). The specimens were attached to a submersible test unit that was retrieved in February 1965. Preliminary examination of the specimens was made aboard ship, and the final examination, tests, and analyses were performed at the Naval Civil Engineering Laboratory.

On recovery, most of the plastic materials

and all of the rope specimens were covered with bacterial slime. Cotton and manila rope specimens were severely deteriorated by marine microorganisms. Wooden test panels, plastics, and manila ropes were attacked by molluscan borers. Glass, metals, natural and butyl rubber, and certain plastic materials were not adversely affected.

The results of breaking-strength tests on ropes, weight loss measurements of wood panels, moisture absorption tests on plastics, and insulation resistance and voltage breakdown tests on electrical insulating materials are presented.

179

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS, PART V. TWO YEARS AT 5,640 FEET. Naval Civil Engineering Lab. Report No. R-495, AD-642 838: November 1966.

As part V of a series of reports on the biological deterioration of materials in the deep ocean, this report covers the data obtained after exposing metallic and nonmetallic specimens for 24 months on the floor of the Pacific Ocean at a depth of 5,640 feet. The test specimens were attached to a submersible test unit that was placed on the sea floor on 2 October 1963 and was recovered on 22 October 1965. Preliminary visual examination of the recovered test specimens was made aboard ship, and the final examination, tests, and analyses of these materials were performed at the Naval Civil Engineering Laboratory.

Most plastic specimens and all rope specimens were covered with bacterial slime. The cotton and manila ropes were severely deteriorated by marine microorganisms. Wood panels and manila ropes were riddled by marine borers. The surface of all the plastic materials in direct contact with wood were deteriorated by these borers. Glass, rubber, and certain plastic materials were not adversely affected.

The results of breaking-strength tests on ropes, hardness and moisture absorption tests on plastics, and insulation resistance and voltage breakdown tests on electrical insulating materials are presented in this report.

180

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS. PART VI. ONE YEAR AT 2,370 FEET. Naval Civil Engineering Lab. Report No. NCEL-TR-525, AD-651 124: 65 p., May 1967.

As Part VI of a series of reports on the

biological deterioration of materials in the deep ocean, this report covers the data obtained after exposing metallic and nonmetallic specimens for 13.4 months on the floor of the Pacific Ocean at a depth of 2,370 feet (test site II). The specimens were attached to a submersible test unit that was emplaced in April 1965 and retrieved in May 1966. Preliminary examination of the specimens was made aboard ship, and the final examination, tests, and analyses were performed at the Naval Civil Engineering Laboratory. On recovery, most of the plastic materials and all of the rope specimens were covered with bacterial slime. Cotton and manila ropes were severely deteriorated by marine microorganisms. Wood panels, certain plastics, and manila ropes were attacked by Molluscan borers. Some of the plastics were attacked by borers directly from seawater environment without the aid of wood bait pieces. Hydroids and tubeworms were found on metal panels. Sea anemone, snails, and crabs were also found attached to various test panels. The surface of a silicone rubber electrical cable insulation was deteriorated by some marine organisms. Typical fouling organisms such as barnacles and bryozoa were not found. Glass, elastomers, and certain plastics were not adversely affected. Data from evaluation of these specimens are presented.

181

Muraoka, J. S. EFFECT OF DEEP OCEAN ORGANISMS ON CONSTRUCTIONAL MATERIALS. In: Proceedings, First Joint Aerospace and Marine Corrosion Technology Seminar, held in Los Angeles, Calif., July 10-12, 1968. p. 115-116, 1968.

182

Muraoka, J. S. DEEP-OCEAN BIODETERIORATION OF MATERIALS - SIX MONTHS AT 6,000 FEET. Naval Civil Engineering Lab. Report No. NCEL-TN-1081, AD-869 397: 45 p., April 1970.

The note reports the data obtained after exposing metallic and nonmetallic specimens for 6.3 months on the floor of the Pacific Ocean at a depth of 6,000 feet (Test site I). The test specimens were attached to a submersible test unit (STU) that was emplaced August 7, 1968 and retrieved on February 12, 1969. Preliminary examination of the specimens was made aboard ship, and the final examination, tests, and analyses were performed at the Naval Civil Engineering Laboratory. Typical fouling organisms such as barnacles, bryozoa, and mussels were not found on test panels exposed at 6,000 feet, but the surfaces of plastics, metals and ropes were coated with a thin film of microbial slime. Untreated wood and ropes made of natural fibers (cotton

and manila) were severely damaged by microorganisms and molluscan borers. Plastic panels which were in direct contact with wood were also affected by the wood borers. Strangely, extensive borer damage to wood panels was restricted to a narrow area extending from the mud-line to a distance of one or two feet above it. Certain chemically treated wood, certain plastics, rubber, and glass were resistant to biodeterioration. Ropes made of polyethylene and polypropylene increased in tensile strength after exposure at 6,000 feet. A limited study on the corrosion of carbon steel and aluminum alloy helped to confirm a long held suspicion that microorganisms might play a role in the corrosion of metals in the ocean.

183

Muraoka, J. S. RELATIONSHIP BETWEEN MARINE FOULING AND CORROSION RATE OF CARBON STEEL AND ALUMINUM ALLOY AT THE SURFACE AND AT 6,000-FOOT DEPTH. Naval Civil Engineering Lab. Report No. NCEL-TR-681, AD-708 012: 57 p., May 1970.

Carbon steel (1010) and aluminum alloy (7178-T6) panels were exposed at the surface (23 to 286 days) and at 6,000-foot depth (189 days) in the Pacific Ocean; (1) to determine the effects of fouling organisms on the corrosion rate and (2) to compare the biological corrosion rate of identical test panels submerged at the two depths. Seawater samples obtained at the surface and at depth were analyzed for dissolved oxygen concentration, PH, salinity and temperature. Bacteriological tests were also conducted on seawater samples. The test panels were submerged in the sea as follows to obtain data on corrosion rates: (1) enclosed inside an initially sterile plastic cylindrical chamber with both ends sealed with membrane filters (control panels), (2) placed inside a cylinder covered with 210-mesh nylon screen cloth, (3) placed inside a cylinder with both ends uncovered, and (4) attached to a phenolic plastic strip (exposed panels). The control specimens became contaminated; however, from corrosion data obtained on test panels exposed on the seafloor in 6,000 feet of water. It is concluded that slime films played a significant role in accelerating corrosion of test specimens. Test panels exposed at the surface corroded at faster rates than replicate test panels which were exposed on the seafloor in 6,000 feet of water. The corrosion rates of both steel and aluminum alloy panels approach constancy after extended exposure in the sea. The various environmental factors and their effects on the corrosion rates

at the surface of the sea and at great depth on the seafloor are discussed.

184

National Bureau of Standards Notes, LONG-TIME EXPOSURE TESTS OF METALS, Journal of the Franklin Institute, 238; No. 3: 212-213, September 1944.

185

NAVAL Applied Science Laboratory, BIBLIOGRAPHY ON MICROBIOLOGICAL CORROSION (DEEP SEA). Report No. TM-1, AD-640 402: 25 p., June, 1965.

The bibliography covers the significant literature on marine microorganisms known to be effective in promoting corrosion and deterioration of materials, with particular reference to microorganisms found in the ocean depths. Brief comments are included for each reference cited except for those significant articles which were not readily obtainable. Papers concerning the effects on high hydrostatic pressures and low ambient temperatures of the ocean depths on the enzymatic mechanisms of certain microbial species are listed for reference in future work along these lines in conjunction with deterioration and corrosion.

186

Naval Civil Engineering Laboratory. EXAMPLES OF CORROSION OF MATERIALS EXPOSED ON STU II-1 IN THE DEEP OCEAN (2340 FEET OF DEPTH FOR 197 DAYS.). Technical Note No. N-695, February 26, 1965.

187

Navy Marine Engineering Laboratory. SEA WATER EXPOSURE TEST OF PURE ALUMINUM COATED STEEL PANELS. Report No. 0400198, AD- 80 430L: July 1955.

188

Niederberger, R. B. CORROSION TESTS OF TYPES 201 AND 202 CR-NI-MN STAINLESS STEELS IN SEA WATER AND MARINE ATMOSPHERE. Naval Engineering Experiment Station. Report No. 91015A, AD-217 455: 13 p., November 1958.

The marine corrosion behavior of Types 201 and 202 chromium-nickel-manganese stainless steels in most respects was similar to that of the corresponding chromium-nickel steels (Types 301 and 302). The chromium-nickel-manganese steels developed light rust and dark brown stains during a 13-mo exposure in a marine atmosphere. No pitting was evident. During sea water immersion, however, the steels sustained severe pitting and worm-holing. For both 201 and 202 alloys, panels in half-hard condition suffered greater weight losses than those in the annealed condition. In addition, unlike

the chromium-nickel steels, they developed stress corrosion cracks along sheared edges and at drilled holes where residual stresses were present. Sensitization at 1200 F for 24 hr lowered resistance to stress corrosion cracking.

189

Niederberger, R. B., Basil, J. L. Bedford, G. T. CORROSION AND STRESS CORROSION OF 5000-SERIES AL ALLOYS IN MARINE ENVIRONMENTS. Corrosion, 22: No. 3: p. 68-73, March 1966.

190

Niederberger, R. B., Ferrara, R. J., Plummer, F. A. CORROSION OF NICKEL ALLOYS IN QUIET AND LOW VELOCITY SEA WATER. Materials Protection and Performance, Vol. 9: No. 8: 1970.

Twenty-two commercially available nickel alloys were subjected to a 2-year investigation. Objectives were to evaluate the relative corrosion behavior of a wide sampling of nickel alloys, and to determine relationships between corrosion resistance and the type and quantity of alloying elements. Data from the investigation were used to arrange the alloys in an order of merit.

191

Nikitina, N. S., Ulanovskii, T. B. SOME DATA ON THE MICROBIOLOGICAL FACTORS OF THE CORROSION OF STEEL IN SEA WATER. Akademiia Nauk SSSR. Murmanskaiia Biologicheskaiia Stantsiia, Dal'niye Zelentsy, Trudy No. 3: 190-200, 1957.

In Russian

Steel samples were immersed in the North Sea for 5, 10, 20 and 150 days during the period of slowest bacterial development from September to January. Bacterial count was 150,000 after 5 days and 310 million per sq cm after 150 days. At 150 days, there were 6,250 aerobic, 250 denitrifying, and 250 x 10<sup>6</sup> anaerobic sulfur bacteria per sq cm. Nitrifying bacteria were not observed. The intensive development of anaerobic bacteria was attributed to the absorption of a relatively immobile layer of water on the steel surface and the exhaustion of oxygen from this layer by the corrosive process.

The effect of aerobic putrefactive bacteria on the corrosion of steel was studied with steel samples exposed to two cultures, one isolated from the corrosion product, the other from sea water. Corrosion rates of samples submerged for 6 mo in sterile sea water were 0.0294, 0.0379, and 0.0366 g per sq m per hr for a bacteria-free control. Samples exposed to the two cultures showed a 20 to 25% in-

crease in corrosion rate. This increase was attributed to increased acidity of the liquid medium and changed electric potential of the metal due to metabolic activity of aerobic bacteria.

192

Nowlan, N. V. INFLUENCE OF WATER MOVEMENT ON CORROSION - NONFERROUS METALS. Corrosion Technology, London. 7: 397-399, December 1960.

193

Oppenheimer, C. H. THE MICROBIAL CORROSION OF IRON. Miami Univ., Inst. of Marine Science. Final Report, Nov. '58 - Dec. '64, AD-653 368: Contract No. Nonr-840(21). 18 p., March 1967.

The investigation showed the potential and magnitude for microbial corrosive effects on iron in marine environments. Aerobic and anaerobic corrosion cells can be developed by a wide variety of microorganisms. Aerobic corrosion is developed through metabolic oxygen consumption by bacteria on localized iron surfaces where organic food is present. Alternating bands of aerobic-anaerobic zones are formed in sediments by layering effects of deposition involving different amounts of organic materials. The layering does produce oxygen differential cells that are very corrosive. Anaerobic corrosion cells are produced by depolarization of the iron due to proton or hydrogen uptake. The activity is proportional to hydrogenase activity or to the presence of hydrogen acceptors in the area. Suitable tests involving weight loss of iron test coupons can be employed to show the corrosive nature of microorganisms in the environment.

194

Orman, M. CORROSION OF ALUMINIUM ALLOYS IN SEA ATMOSPHERES. Prace Inst. Hutniczych, 13: 225-227, 1961.

In Polish with English summary

Two aluminum-manganese and seven aluminum-magnesium alloys were exposed 2 m below the sea surface and on a pier of a Baltic harbor for 8 yr. Samples were 2 mm thick sheet, either cold-rolled or annealed. The manganese alloys (samples A and B) contained 1.35 and 1.22% manganese and were stabilized with 0.13 and 0.30%, respectively, of titanium. Five of the magnesium alloys contained about 3% magnesium, and either chromium, chromium + manganese, or chromium + vanadium as stabilizers (samples C, D, E, F, and K). The remaining two alloys contained 5% magnesium with manganese + chromium as

stabilizers (samples G and H). The extent of corrosion was evaluated from loss of tensile strength and elongation, expressed as percentage loss per year.

The results of 8 yr tests are tabulated. Based on tensile strength losses, all alloys, with the exception of alloy K (5% magnesium, 0.07% manganese, and 0.25% chromium), have good resistance to sea water. Aluminum-manganese alloys are less resistant than aluminum-magnesium alloys. Alloy H (5% magnesium, 0.25% manganese, and 0.30% chromium) has high resistance to corrosion and is recommended for construction of sea-going vessels. Elongation decreased more rapidly than tensile strength. Alloys C and H had the lowest rate of elongation loss (not > 4%/yr); alloys A and B had the highest ( $\leq 11$  and 7%, respectively). Alloy F (3% magnesium, 0.34% chromium, and 0.34% vanadium) had the lowest rate of tensile strength loss (a maximum of 0.44%/yr for cold-rolled samples and 0% for annealed samples). The corrosion rate of alloys exposed to marine atmosphere was generally higher than in immersion tests; like the latter, elongation losses exceeded losses of tensile strength. Alloy H was highly resistant. Manganese, chromium, and vanadium additives appear effective in increasing the corrosion resistance of aluminum-magnesium alloys when their total content is at least 0.5%. Thus, alloy H, containing 0.55% of chromium + manganese, is more resistant than alloy G, containing only 0.42% of the same components. Among the magnesium alloys with 3% magnesium, alloy F, containing 0.68% of chromium + vanadium, is the most resistant. Considering the relatively high rate of mechanical strength loss of alloys A and B, aluminum-manganese alloys are unsuitable for use in a marine atmosphere.

195

Pavlov, S. E. CORROSION OF ALUMINUM ALLOYS UNDER SEA CONDITIONS. Akademiia Nauk SSSR. Komissii PO Bor'be S Korroziei Metallov, Trudy, No. 1: 58-75, 1951.

In Russian

196

Pelzel, E. CORROSION BEHAVIOR OF SPECIAL CAST BRASS ALLOYS. Metal, 7: 767-771: October 1953.

In German

Aluminum brasses containing 0.31-1.54% iron, 0.31-1.26% manganese, and 0.30-1.50% nickel, silicon brasses with small additions of lead, arsenic, manganese, and nickel; and copper-zinc alloys of 50-60%

copper content with additions of nickel and tin were tested for corrosion resistance in a solution of 3% sodium chloride plus 0.1% hydrogen peroxide. In addition the aluminum brasses were also tested in 10% hydrochloric acid and artificial sea water.

In the artificial sea water tests, addition of 0.4-0.6% iron and manganese to brass containing 1.16-1.74% aluminum had the same corrosion-inhibiting effect as had 1% nickel. A combination of nickel and manganese was not noticeably better than nickel alone. Tin bronze again showed inferior resistance to unalloyed and special alloy brasses. Tinned brass, which offered no resistance to attack by hydrochloric acid, showed remarkable resistance to artificial sea water.

197

Peterson, M. H., Waldron, L. F. INVESTIGATION OF MILD STEEL CORROSION RATE IN SAN DIEGO HARBOR. Corrosion, 17: No. 4: 112, April 1961.

198

Peterson, M. H., Lennox, T. THE CORROSION BEHAVIOR OF STAINLESS STEELS IN SEA WATER. Naval Research Lab. Report No. NRL-MR-1795, AD-657 938: 33 p., June 1967.

The corrosion behavior of several series of stainless steels is discussed. Photographs of typical attack in both experimental panels and operational equipment are shown. Because of the susceptibility of stainless steel to pitting, its use in sea water should be avoided in new designs. The 300 series, however, may be used if provided with cathodic protection. The 400 series stainless steels are unsuitable for use in sea water even if provided with cathodic protection.

199

Peterson, M. H., Lennox, T. J., Groover, R. E. A STUDY OF CREVICE CORROSION IN TYPE 304 STAINLESS STEEL. In: Proceedings of National Association of Corrosion Engineers, Twenty-Fifth Conference, Held in Houston Tex., March 10-14, 1969. p. 314-317, 1970.

The study described in this paper was initiated to determine the reliability of cathodically protected Type 304 stainless steel O-ring seals in sea water. The corrosion of cathodically protected and unprotected flange type O-ring seals was studied both in quiescent sea water and in sea water with a flow rate of 1:2 foot per second. At the conclusion of the immersion phase of the experiment some preliminary measurements were made to gain insight into the solution chemistry of the corrodent in

differential aeration cells on stainless steel.

200

Peterson, V. C., Tamor, David. TESTS SHOW HOW SEA WATER AFFECTS WIRE-STRAND AND ROPE. Materials Protection, 7: No. 5: 32-34, May 1968.

Tests were conducted to determine the relative corrosion resistance of aluminumized strand and wire rope, austenitic stainless steel, galvanized wire, and copper-nickel clad Type 304 stainless in sea water. The tests were conducted at Woods Hole, Mass. and in the warmer waters of Wrightsville Beach, N. C. and Boca Raton, Fla. Visual examinations were made periodically and strengths reported after exposures of up to 596 days. Specimens were exposed to the atmosphere, partial immersion, total immersion, and to mud zone environments.

201

Plummer, F. A. SEA-WATER CORROSION CHARACTERISTICS OF NICKEL-BASE ALLOYS. Naval Ship Research and Development Lab. Report No. MATLAB-297, AD-854 698L: 38 p., May 1969.

202

Porte, H. A. THE EFFECT OF ENVIRONMENT ON THE CORROSION OF METALS IN SEA WATER - A LITERATURE SURVEY. Naval Civil Engineering Lab. Report No. NCEL-TN-907, AD-820 155L: 27 p., July 1967.

203

Prochko, R. J., Myers, J. R., and Saxer, R.K. CORROSION OF BERYLLIUM BY SALT WATER. Mat. Prot., Vol. 5: No. 12: December 1966.

Chloride in aqueous environments has a deleterious corrosive effect on beryllium. Tests with pickled and anodized specimens of sheet beryllium reveal its use is limited by pitting attack and stress-corrosion failure. This paper describes experiments in five environments: distilled water, synthetic sea water, natural sea water, 3 percent NaCl solution and 3.5 percent NaCl solution.

204

Rausch, M. W. SALT WATER CORROSION TESTS OF ALUMINUM CASTING ALLOYS, TERNALLOY 5 TERNALLOY 7. Navy Marine Engineering Lab. Report No. 040037A 7, AD-102 079L: v.p., April 1956.

205

Rausch, M. W. SEA WATER CORROSION RESISTANCE AND TENSILE PROPERTIES OF ALUMINUM ALLOY 6066-T6 EXHIBITED BY HARVEY ALUMINUM CORPORATION LOS ANGELES, CALIFORNIA.

Navy Marine Engineering Lab.  
Report No. 910037A, AD-213 737L: v.p.,  
February 1958.

206

Redfield, A. C., Weiss, C. M. THE RESISTANCE OF METALLIC SILVER TO MARINE FOULING. Biol. Bull., 94: No. 1: 25-28, February 1948.

A specimen of coin silver, which contains about 10% copper, remained entirely free of fouling throughout an exposure of 1 yr in the sea at Miami Beach, Fla. Two panels of pure silver began to foul within 1 - 2 mo, and both were completely covered at the end of 4 mo of exposure. One of the pure silver specimens had been pre-soaked in sea water 2 mo prior to test; the corrosive coating thus formed resisted fouling during the early months of exposure better than a clean surface of bright silver. Coin silver is believed to be more resistant than pure silver to fouling because of its higher rate of solution when exposed in the sea.

There was no indication that the surface of silver from which solution was prevented by coupling with zinc or iron had any anti-fouling effect; pure silver specimens thus treated fouled heavily during the first month of the 12-mo test period. Silver coupled to nickel showed slight resistance to fouling only during the first 2 mo; contact with copper had scarcely any effect. The results were proportional to the differences in potential of the coupled metals.

207

Reed, S. A. CORROSION OF CARBON AND ALLOY STEELS IN WATER AND SEAWATER. Oak Ridge National Lab. Report TM-1612: Contract W-7405-eng-26: 20 p., October 1966.

Current knowledge of factors that govern corrosion and service life of steel in sea water evaporation environments is summarized. Some data from OSW research and development reports are included. It is concluded information currently available is inadequate to provide any reliable estimate of life expectancy of carbon steel in sea water evaporator environments. Additional testing is necessary at lower dissolved oxygen levels to determine more precisely role of oxygen in corrosion of steel in hot sea water and brine.

208

Reinhart, F. M. PRELIMINARY EXAMINATION OF MATERIALS EXPOSED ON STU 1-3 IN THE DEEP OCEAN, (5640 FEET OF DEPTH FOR 123 DAYS). Naval Civil Engineering Lab. Report No. NCEL-TN-605, AD-601 892: 34 p., June, 1964.

Preliminary results of corrosion of materials, based solely upon visual examinations, exposed in 5640 feet of water in the Pacific Ocean for 123 days showed only a few cases of deterioration different from those usually found in moving surface sea water. The clad layers on two aluminum alloys corroded at a much faster rate than normal for surface sea water. The lace-work and undersurface types of attack on certain stainless steels appear to be similar to types of attack by stagnant surface sea water; this could be attributed to low oxygen content as well as lack of a significant movement of deep sea water. Other materials, both metallic and non-metallic were not seriously deteriorated and some showed absolutely no evidence of deterioration.

209

Reinhart, F. M. EXAMPLES OF CORROSION OF MATERIALS EXPOSED ON STU II-1 IN THE DEEP OCEAN (2340 FEET OF DEPTH FOR 197 DAYS). Naval Civil Engineering Lab. Report No. NCEL-TN-695, AD-614 903: 52 p., February 1965.

Preliminary results of corrosion of materials, based solely upon visual examinations, exposed in 2340 feet of water in the Pacific Ocean for 197 days showed only a few cases of deterioration different from those usually found in moving surface sea water. The clad layers on two aluminum alloys corroded at a much faster rate than normal for surface sea water. The lace-work and undersurface types of attack on certain stainless steels appear to be similar to types of attack by stagnant surface sea water; this could be attributed to low oxygen content as well as lack of a significant movement of deep sea water. Other materials, both metallic and nonmetallic, were not seriously deteriorated and some showed absolutely no evidence of deterioration. In order to obtain meaningful results, considerable critical examination of the various specimens will be required.

210

Reinhart, F. M. DEEP OCEAN CORROSION. Geo-Marine Technology, 1; No. 9: 15-26, September 1965.

211

Reinhart, F. M. EFFECT OF DEEP OCEAN ENVIRONMENTS ON THE CORROSION OF SELECTED ALLOYS. Naval Civil Engineering Lab. Report No. NCEL-TN-781, AD-626 586: 32 p., October 1965.

This is a partial report covering eight materials selected as representative of

the different classes of alloys exposed in the Pacific Ocean at depths ranging from 2340 to 5640 feet for periods of time ranging from 123 to 1064 days. Aluminum alloy, 5086-H34, was attacked by intergranular corrosion which was manifested by pitting and edge penetration. It was also attacked by crevice corrosion. Its corrosion rates and pit depths increased with time of exposure. Copper alloy No. 715, alloy steel AISI 4130 and the extra high strength low alloy steels corroded uniformly; their corrosion rates decreasing with increasing time of exposure regardless of depth. The nickel base alloy, Hastelloy C, was uncorroded. The austenitic stainless steel, 20-CB, also was uncorroded except for crevice corrosion after 197 days of exposure at a depth of 2340 feet. No significant effect of pressure on the corrosion behavior of these alloys is evident from the data presented.

212

Reinhart, F. M. VISUAL OBSERVATIONS OF CORROSION OF MATERIALS ON STU I-1 AFTER 1064 DAYS OF EXPOSURE AT A DEPTH OF 5300 FEET IN THE PACIFIC OCEAN. Naval Civil Engineering Lab. Report No. NCEL-TN-793, AD-643 490: 50 p., November 1965.

Visual observations of materials exposed on the bottom of the Pacific Ocean at a depth of 5300 feet for 1064 days showed that the corrosion of most of the alloys in the mud was different from the corrosion in the water 6 feet to 10 feet above the bottom. The stainless steels exhibited a honey-comb type of attack very similar to the type of attack by stagnant surface sea water. The 5000 series aluminum alloys showed deep pitting; this could be explained on the basis of the low oxygen content combined with the nearly stagnant condition of the sea water. The 70% Ni-30% Cu alloy which was partially embedded in the sediment showed pitting that undoubtedly was caused by the composition of the peculiar environment in the water-sediment interfacial zone. The plastic materials were unaffected except those portions encased in wood which were attacked by wood boring animals. Hydroids attached themselves to and grew on both metallic and non-metallic materials with no apparent deteriorative effects.

213

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE. Naval Civil Engineering Lab. Report No. NCEL-TR-504, AD-644 473: 117 p., December 1966.

A total of 1,590 specimens of 107 different alloys were exposed at depths of 2,340, 5,300, and 5,640 feet at two sites in the Pacific Ocean for 197, 1,064, and 123 days to determine the effects of deep ocean environments on the corrosion of materials. The corrosion rates, pit depths, types of corrosion, changes in mechanical properties, and analyses of corrosion products of the alloys are presented. Titanium alloys and two nickel base alloys (Ni-Fe-Cr-825 and Ni-Mo-Cr-'C') were immune to corrosion. The corrosion rates of copper alloys and steels decreased with a decrease in the oxygen concentration of the seawater and with increasing time of exposure at a nominal depth of 5,500 feet. The corrosion rates of most of the aluminum alloys increased with increasing time of exposure and with decreasing oxygen concentration of seawater. Muntz metal, and nickel-manganese bronze were attacked by dezincification and aluminum bronze by dealuminification. All the stainless steels except types 316 and 316L, 20-Cb and 17 Cr - 7 Ni - 0.7 Ti - 0.2 Al were attacked by pitting corrosion. Only two precipitation hardened stainless steels were susceptible to stress corrosion cracking. The oceanographic parameters varied with depth. Changes in temperature and oxygen concentration exerted the most influence on the corrosion of the alloys.

214

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE. In: Proceedings 4th. U.S. Navy Symposium on Military Oceanography. (Held at the Naval Research Laboratory, Wash. D.C. May 1967.) 1: p. 265-288, 1967.

Presents results of the evaluation of the irons, steels, low alloy steels, alloy cast irons, metallic coated steel, uncoated and metallic coated steel wire ropes and anchor chains for six exposure periods and two nominal depths: NCEL's STU program to establish the best materials to be used in deep ocean construction considers simple corrosion as well as stress corrosion. The corrosion rates of all the alloys decreased asymptotically with time, and became constant at rates varying between 0.5 and 1.0 MPY after three years of exposure at 5500 feet. These rates are about 1/3 those of wrought steels at the surface, and at 2350 feet were lower than those at 5500 feet and decreased with time. Additional detailed results are delineated.

215

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE - PART I. IRONS, STEELS, CAST

IRONS, AND STEEL PRODUCTS. Naval Civil Engineering Lab. Technical Note No. TN-900: 75 p., July 1967.

A total of 1300 specimens of 47 iron base alloys were exposed at depths of 2,340, 2,370, 5,300, 5,640 and 6,780 feet at two sites in the Pacific Ocean for 197, 402, 1064, 123, 751 and 403 days respectively to determine the effects of deep ocean environments on their corrosion behavior. Corrosion rates, pit depths, types of corrosion, changes in mechanical properties, effects of stress, and analyses of corrosion products are presented. The Corrosion rates of all the alloys, both cast and wrought, decreased asymptotically with duration of exposure and became constant at rates varying between 0.5 and 1.0 mils per year after three years of exposure in sea water and partially embedded in the bottom sediments at a nominal depth of 5,500 feet. These corrosion rates are about one-third those at the surface in the Atlantic Ocean. At the 2,350 foot depth, the corrosion rates in sea water also decreased with duration of exposure but tended to increase slightly with duration of exposure in the bottom sediments. The corrosion rates at the 2,350 foot depth were less than those at the 5,500 foot depth. The mechanical properties were unimpaired. Silicon and silicon-molybdenum cast irons were uncorroded. A sprayed 6 mil thick coating of aluminum protected steel for a minimum of three years and a hot dipped 4 mil thick coating of aluminum protected steel for a minimum of 13 months while a hot dipped 1.7 mil thick coating of zinc protected steel for about 4 months.

216

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE. PART II - NICKEL AND NICKEL ALLOYS. Naval Civil Engineering Lab. Report No. NCEL-TN-915, AD-821 256: 65 p., August 1967.

A total of 635 specimens of 75 different nickel alloys were exposed at two different depths in the Pacific Ocean for periods of time varying from 123 to 1064 days to determine the effects of deep ocean environments on their corrosion resistance. Corrosion rates, types of corrosion, pit depths, effects of welding, stress corrosion cracking resistance, changes in mechanical properties and analyses of corrosion products of the alloys are presented. Of those alloys tested, the following were practically immune to corrosion: nickel-chromium-iron alloy 718; nickel-iron-chromium alloys, except 902; nickel-chromium-molybdenum alloys; nickel-cobalt-chromium alloy; nickel-chromium-

iron-molybdenum alloys; nickel-chromium-cobalt alloy; and nickel-molybdenum-chromium alloy. Alloys attacked by uniform or general corrosion were the cast nickel-copper alloys; nickel-molybdenum-iron alloy and nickel-molybdenum alloy. Alloys attacked by crevice or pitting corrosion were the nickels; wrought nickel-copper alloys; nickel-chromium-iron alloys except 718; nickel-iron-chromium alloys 902; nickel-tin-zinc alloy; nickel-beryllium alloy; nickel-chromium alloys; and nickel-silicon alloy.

217

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE. PART III - TITANIUM AND TITANIUM ALLOYS. Naval Civil Engineering Lab. Technical Note N-921, AD-821 257L: 31 p., September 1967.

A total of 475 specimens of 10 titanium alloys were exposed at two different depths in the Pacific Ocean for six different periods of time varying from 123 to 1064 days to determine the effects of deep ocean environments on their corrosion resistance. Specimens of the alloys were also exposed in surface seawater for 181 days for comparison purposes. Corrosion rates, types of corrosion, pit depths, effects of welding, stress corrosion cracking resistance and changes in mechanical properties are presented. The alloys were immune to corrosion and stress corrosion cracking except alloy 13V-11Cr-3Al with unrelieved circular welds. This alloy with unrelieved circular welds failed by stress corrosion cracking after 181 days of exposure at the surface, 403 days at 6,780 feet and 402 days at 2,370 feet. The 13V-11Cr-3Al alloy with unrelieved butt welds failed by stress corrosion cracking when stressed at 75 percent of its yield strength after 35, 77 and 105 days of exposure at the surface. The mechanical properties of the alloys were not affected. Some information from TOTO in the Atlantic Ocean is included for comparative purposes.

218

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE - PART IV. COPPER AND COPPER ALLOYS. Naval Civil Engineering Lab. Technical Note No. N-961, AD-835 104: 58 p., April 1968.

A total of 1050 specimens of 46 different copper alloys were exposed at two depths, 2,500 and 6,000 feet, in the Pacific Ocean for periods of time varying from 123 to 1064 days in order to determine the effects of deep ocean environments

on their corrosion resistance. Corrosion rates, types of corrosion, pit depths, stress corrosion cracking resistance, changes in mechanical properties and analyses of corrosion products of the alloys are presented. Copper, beryllium-copper, arsenical admiralty brass, aluminum brass, nickel brass, G bronze, modified G bronze, M bronze, leaded tin bronze, phosphorous bronze A, phosphorous bronze D, nickel-aluminum bronzes, Ni-Vee bronze A, Ni-Vee bronze B, Ni-Vee bronze C, copper-nickel alloys 95-5, 80-20, 70-30 containing 0.5 percent iron, 70-30 containing 5 percent iron, 55-45, nickel-silver containing 18 percent nickel, and Cu-Ni-Zn-Pb corroded uniformly and were low, 1 MPY or less after 1 year at a depth of 2,500 feet and after 2 years at a depth of 6,000 feet. The remainder of the alloys were attacked by selective corrosion; commercial bronze, red brass, yellow brass, Muntz metal, Naval brass, manganese bronze, nickel-manganese bronze, wrought 5 and 7 percent aluminum bronzes, cast 10, 11 and 13 percent aluminum bronzes, 3 percent silicon bronze and silicon bronze A. The copper alloys were not susceptible to stress corrosion cracking. Only the mechanical properties of the alloys attacked by selective corrosion were adversely affected. The corrosion products consisted of cupric chloride, copper hydroxide-chloride, metallic copper, copper oxy-chloride and nickel hydroxide.

219

Reinhart, F. M. CORROSION OF DSRV MATERIALS IN SEA WATER - 3 MONTHS EXPOSURE. Naval Civil Engineering Lab. Report No. NCEL-TN-1007, AD-682 954: 23 p., January 1969.

A sea water exposure program was initiated to determine the effects of galvanic and crevice corrosion on selected combinations of alloys; and the efficacy of sealing compounds, paint coatings and galvanic anodes for preventing corrosion, crevice corrosion and galvanic corrosion.

220

Reinhart, F. M. CORROSION OF MATERIALS IN HYDROSPACE - PART V. ALUMINUM ALLOYS. Naval Civil Engineering Lab. Technical note No. N-1008, AD-683 334: 87 p., January 1969.

A total of 900 specimens of 40 different aluminum alloys were exposed at depths of 2,500 and 6,000 feet in the Pacific Ocean for periods of time varying from 123 to 1064 days in order to determine the effects of deep ocean environments on their corrosion resistance. Corrosion rates, types of corrosion, pit depths, stress

corrosion cracking resistance, changes in mechanical properties and compositions of corrosion products are presented. Alloys 2219-T87, 7079-T6, 7178-T6 and Alclad 7079-T6 were susceptible to stress corrosion cracking. Alloys 2024-T3, 7039-T6, 7075-T6, 7079-T6 and 7178-T6 were attacked by the exfoliation type of the corrosion. All the alloys were attacked by pitting and crevice types of corrosion. With reference to aluminum alloys, sea water at depth was more aggressive than at the surface and the bottom sediments were more corrosive than the sea water at depth in the Pacific Ocean. Aluminum alloys not susceptible to stress corrosion cracking and exfoliation corrosion can be used for deep sea applications if adequately protected and if brought to the surface periodically for maintenance of the protective system.

221

Reinhart, F. M. CORROSION OF MATERIALS IN SURFACE SEA WATER AFTER 6 MONTHS OF EXPOSURE. Naval Civil Engineering Lab. Technical Note No. N-1023, AD-684 081: 39 p., March 1969.

A total of 880 specimens of 215 different alloys were completely immersed in surface sea water for six months to obtain data for comparison with deep ocean corrosion data. Corrosion rates, types of corrosion, pit depths, and changes in mechanical properties were determined. The highly alloyed nickel alloys, titanium alloys, silicon cast irons, specialty stainless steels, columbium, tantalum and tantalum-tungsten alloy were uncorroded both at the surface and at depth. The corrosion rates of the copper base alloys, nickel base alloys, steels, and cast irons decreased as the concentration of oxygen in sea water decreased. The copper base alloys, steels, cast irons, molybdenum, tungsten, leads and lead-tin solder corroded uniformly. All the aluminum alloys were attacked by pitting and crevice corrosion and sea water was more aggressive at depth than at the surface. The effect of the oxygen concentration of sea water on the corrosion of aluminum alloys was inconsistent. The stainless steels were attacked by crevice, pitting, edge and tunnel corrosion except types 310, 317 and 329, 20Cb, 20Cb-3 and AM350 on which there was only incipient crevice corrosion. Crevice corrosion was more severe in surface waters than at depth.

222

Reinhart, F. M. CORROSION OF DSRV MATERIALS IN SEA WATER - SIX MONTHS EXPOSURE. Naval Civil Engineering Lab. Report No. NCEL-TN-1037, AD-857 325: 31 p., July 1969.

In order to provide information needed about specific corrosion problems involved with the design of the DSRV, a sea water exposure program was initiated to determine: the galvanic and crevice corrosion on selected combinations of alloys and the efficacy of sealing compounds, paint systems and sacrificial anodes as protective measures.

223

Reinhart, F. M. CORROSION OF DSRV MATERIALS IN SEA WATER - 12 MONTHS NATURAL EXPOSURE AND 98 CYCLES IN PRESSURE VESSELS. Naval Civil Engineering Lab. Report No. NCEL-TN-1096, AD-871 192L: 44 p., May 1970.

In order to evaluate specific corrosion problems involved in the design of the DSRV (Deep Submergence Rescue Vessel), a corrosion test program was initiated to determine: (1) the effects of galvanic and crevice corrosion on selected combinations of metals, and (2) the efficacy of selected paint coatings, sealing compounds and galvanic anodes for mitigating corrosion, crevice corrosion and galvanic corrosion. Composite specimens representative of proposed DSRV construction materials and methods were exposed for 370 days at mean tide level in sea water and to cyclic exposure to pressurized sea water. This report presents an evaluation of these composite specimens after exposure.

224

Reinhart, F. M. CORROSION OF MATERIALS IN SURFACE SEA WATER AFTER 6 MONTHS OF EXPOSURE. Naval Civil Engineering Lab. Report NCEL-TN-1023, AD-684 081: 77 p., March 1969.

A total of 880 specimens of 215 different alloys were completely immersed in surface sea water for six months to obtain data for comparison with deep ocean corrosion data. Corrosion rates, types of corrosion, pit depths, and changes in mechanical properties were determined.

225

Rice, E. F. T. A METHOD OF CONSIDERING COSTS WHILE SELECTING MATERIALS FOR CORROSION SERVICE. Corrosion, 10: p. 252, August 1954.

A suggested corrosion-rating guide for three price classes of metals and alloys lists three permissible and one prohibitory corrosion-rate levels in order of increasing penetration (in inches per year). This arrangement of resistance merit v. cost permits the selection of materials for anticorrosive service within justified cost

limits. Absolute performance, however, must be determined by actual field tests.

Class I metals, which comprise relatively expensive materials such as silver, tin, Hastelloys, Chlorimets, Ilium, and titanium, are entirely satisfactory for corrosion losses of 0-0.003 ipy. They should be used with caution at 0.003-0.006 ipy penetrations, only under special conditions for short exposures where penetration attains 0.006-0.010 ipy, and not at all where corrosion rates exceed 0.010 ipy. Class II materials, comprising metals and alloys of intermediate cost such as stainless steels, Monels, nickel, Inconel, Durimets, Everdur, Duriron, Durichlor, Stellite, copper, magnesium, bronzes and aluminum, are suitable for use where corrosion losses are 0-0.005 ipy; they are applicable with caution between 0.005-0.012 ipy and for short exposure between 0.012-0.020 ipy, but not for corrosion losses above 0.020 ipy. Use of Class III materials, which include the few relatively cheap metals such as steel, cast iron, lead, brass, and zinc, is justified for corrosion losses up to 0.009 ipy. They can be used with caution between 0.009-0.030 ipy, and for short terms at 0.030-0.055 ipy, but not at all where penetration exceeds 0.055 ipy. In all three cost classes, the incidence of pitting invalidates these limits and justifies application only under special conditions for short exposures. For platinum, gold, tantalum, and zirconium, Class I limits should be divided by 5.

All given limits are conservative figures developed from a study of the corrosion literature and from analyses of hundreds of laboratory and plant tests over a period of 12 yr.

226

Richards, John T. THE CORROSION OF BERYLLIUM COPPER STRIP IN SEA WATER AND MARINE ATMOSPHERES. Am. Soc. Testing Materials, Proc. 53: p. 911-929, 1953.

The corrosion resistance of beryllium copper was found to compare favorably with that of copper under many conditions of sea water or marine atmosphere exposure and can be considered for marine applications requiring high strength and the corrosion resistance of copper.

Beryllium copper and beryllium-cobalt-copper in various tempers and conditions were exposed to sea water and marine atmospheres at Harbor Island and Kure Beach, N.C. For comparative purposes, samples (in the annealed condition) of

phosphorus deoxidized copper, arsenical admiralty, iron-modified 70-30 cupro-nickel, and phosphor bronze (Grade A) were included in many of the tests. Weight losses and decreases in strength and elongation for test periods up to 2 yr were determined.

In quiet sea water, the corrosion resistance of beryllium copper was less than that of cupro-nickel but equal to that of copper or admiralty. With increasing water velocities, the resistance offered by beryllium copper was still less than cupro-nickel but superior to copper or admiralty. In flowing sea water, partial immersion or waterline effects caused no appreciable change in corrosion rate.

High-velocity tests, such as rotating-spindle, Engineering Experiment Station (EES), and jet impingement, yielded slightly anomalous results. For example, beryllium copper was more resistant to corrosion in the rotating spindle and EES tests than in the sea water jet test. Under open-circuit and polarizing conditions, galvanic potential and corrosion were similar to the values obtained with other copper-base materials.

Beryllium copper offered better resistance to corrosion by marine atmospheres than either copper or phosphor bronze. The corrosion rate at 80 ft from the sea was substantially greater than at 800 ft. It also provided slightly better resistance to sea water or marine atmosphere than did beryllium-cobalt-copper. Although cold rolling or precipitation hardening caused a marked improvement in the strength of these alloys, material condition exerted no observable influence upon corrosion resistance. For all materials, the corrosion rate decreased with increasing exposure time but increased, often rapidly, with a rise in velocity. Test results are in fair agreement with those of other investigators. In several instances data do not agree with service experience.

227

Rigo, J. H. SEA WATER TESTS DETERMINE CORROSION RESISTANCE OF STRANDED STEEL WIRE. Materials Protection, 1: p. 28-33, 36-37, July 1962.

Stressed and unstressed specimens of single and stranded steel wire were exposed 13 mo in the ocean at Wrightsville Beach, N.C. Wires were fully immersed; the 15-ft stranded samples were anchored in the mud at one end and exposed to the atmosphere at the other.

Represented were Bright Mild Plow and Bright Monitor steels, with and without various coatings, and two stainless steels. Some specimens were cathodically protected at two levels by magnesium anodes.

Susceptibility to pitting renders AISI Type 316 and USS Tenelon stainless steel strands unsuitable for long-term continuous service without cathodic protection. Zinc coated steel wires corrode only superficially; cathodic protection or an extruded poly(vinyl chloride) covering extends the life of single wire or strands. Aluminized steel may outperform zinc coated items of comparable coating thickness. Cathodic protection, however, removes aluminum faster than the zinc and advantages of aluminizing remain doubtful. Single wires corrode faster and differently than stranded specimens. Stainless steel single wires show no pitting but strands and cable do.

228

Rigo, J. H. CORROSION RESISTANCE OF STRANDED STEEL WIRE IN SEA WATER. *Materials Protection*, 5: No. 4: 54-58, April 1966.

229

Rogers, T. H. A METHOD FOR ASSESSING THE RELATIVE CORROSION BEHAVIOUR OF DIFFERENT SEA-WATERS. *J. Inst. Metals*, 76: p. 597-611, February 1950.

The Copper Corrosion Index (C.C.I.) test was developed to evaluate the relative corrosiveness of sea waters toward copper-base alloys. The C.C.I. is the average amount of copper, in milligrams, corroded from three specimens of 16-gauge copper 0.25 dm sq during 22 hr in 350 ml sea water at 20 C, aerated by a constant jet of filtered air. The C.C.I. values range from 3 to 30; high values are usually associated with high corrosiveness. Comparisons between alloys should be made in the same sea water, preferably in a C.C.I. range of 12-18.

Corrosive behavior of sea water varies widely with the time of year, the locality at which the water sample is taken, and the length of time the sample is stored before use. Corrosiveness is not readily shown by ordinary chemical tests. Small amounts of contaminants produced by biological activity are important factors that are not readily analyzed and that may retard as well as accelerate corrosion. Salinity and pH are fairly constant and are not important. Corrosive activity does not correlate with polarographic measurements, electrode potentials or

polarization curves.

Sea-water corrosion of copper-base alloys is associated with the formation and breakdown of metal surface films, which can be detected by low-power microscopic examination. Sea waters having high C.C.I. values tend to form films on the alloy that may inhibit attack, cause highly localized corrosion, or blister and cause accelerated attack. In such exposure, low-power microscopic examination should supplement the C.C.I. determinations. Sea waters having a low C.C.I. give less visible evidence of film formation and cause widespread attack on alloys inclined to undergo impingement attack in service, but little or no attack on alloys known to be resistant in service. Certain copper-base alloys are more resistant than others to changes in C.C.I., and these usually behave well in service. Aluminum brass and cupro-nickel (70Cu-30Ni-0.5Fe) show little corrosion in waters having a C.C.I. below 20. Admiralty metal and cupro-nickel (70Cu-30Ni-0.04Fe) are very sensitive to change in C.C.I.

All-around resistance of an alloy can be assessed only by testing in different sea waters. The addition of iron salts to sea water decreases the C.C.I. and tends to make it more constant, although this effect may not be permanent.

230

Rogers, T. H. THE CORROSION BEHAVIOUR OF NON-FERROUS METALS IN SEA WATER. *Trans. Inst. Marine Engrs. (Canadian Div. Supplement)*. No. 2: p. 31-37, December 1960.

Survey of the sea water corrosion resistance of aluminum alloys, brasses, bronzes, cupro-nickel alloys, Cu-Ni-Fe alloys, gun metals, Cu, Monels and Sn and Pb alloys.

231

Rogers, T. H. MARINE CORROSION HANDBOOK. New York, McGraw-Hill, 1960.

232

Rogers, T. H. MARINE CORROSION. London, George Newnes, 1968.

233

Rowlands, J. C. STAINLESS STEELS AND RELATED ALLOYS VERSUS MARINE ENVIRONMENTS. *Corrosion Technol.*, 6: p. 359-363, December 1959.

Sheet specimens of seven martensitic, one ferritic, and nine austenitic stainless steels plus four high-nickel alloys in seven different surface conditions were

fully immersed in sea water for 3 to 20 mo. Similar panels, in the bright surface condition, were subjected up to 9 yr to half-tide immersion and marine atmospheres. In addition, crevice corrosion rigs (using a flat piece of Perspex to simulate crevices) were immersed in sea water for 30 mo, and galvanic corrosion trials were conducted with stainless steels coupled to graphite, copper, and mild steel.

All alloys tested, except in crevices, showed good intrinsic corrosion resistance to sea water. The austenitic steels, especially an 18/8 chromium-nickel steel containing 2.5% molybdenum, were the least susceptible to crevice corrosion but no alloy was immune. The slightly higher corrosion rates exhibited by rough surface finishes may have been caused by greater attraction of barnacles for such surfaces, with a resulting greater tendency toward crevice formation. Crevice gaps had to be extremely small for maximum corrosion to occur. The passive surface oxide film, upon which stainless alloys rely for their corrosion resistance, probably did not fail mechanically but was damaged by an electrochemical process, whereupon crevice corrosion proceeded because of differential aeration.

Under half-tide conditions, crevice corrosion again was the major form of damage. It was less severe, however, than under full immersion, probably because the surface oxide film had time to heal (re-anneal) while the specimens were dry. Samples exposed to atmospheric conditions showed no significant corrosion, but all surfaces were tarnished, and all steels showed a tendency to rust. In general, the most corrosion resistant were the austenitic alloys, followed by the martensitic alloys; the high-nickel alloys were slightly better than the ferritic alloy. In resistance to crevice corrosion, austenitic steels again headed the list, followed by high-nickel alloys, the martensitic steels being less resistant than the ferritic steel.

234

Rowlands, J. C. PREFERENTIAL PHASE CORROSION OF NAVAL BRASS IN SEA WATER. In: Proceedings, 2nd. International Congress on Metallic Corrosion, New York, N.Y., March 11-15, 1963. p. 795-800, 1963.

235

Rozenberg, L. A. ROLE OF SULFATE-REDUCING BACTERIA ON THE CORROSION OF LOW-ALLOY AND STAINLESS STEEL IN SEA WATER.

Akad. Nauk SSSR. Inst. Okeanol., Trudy 49: p. 258-265, 1961.

In Russian

Weighed samples of a stainless steel and a low-alloy steel unprotected and coated with a red lead anticorrosive paint were suspended in flasks containing sterile artificial sea water with sodium formate added (as a source of carbon) and in flasks containing the same medium inoculated with a pure culture of Vibrio desulfuricans. The flasks were incubated for 6 mo under anaerobic conditions at 25 to 27 C.

On the unprotected low-alloy steel, the numbers of microorganisms at 6 mo reached 1.4 to 2.3 million/cm<sup>2</sup>, and the concentration of hydrogen sulfide 80 to 160 mg/liter. On the coated low-alloy steel 0.5 to 0.6 million/cm<sup>2</sup> cells were present; the hydrogen sulfide concentration was 45 to 60 mg/liter. These lower values are attributed to the toxic effect of the paint. Low-alloy steel in both sterile and inoculated flasks began to corrode after ~ 10 days incubation. In sterile flasks, the initial rate was 0.02 to 0.03 gm/cm<sup>2</sup>/hr; after 6 mo, it was 0.008 to 0.014 gm/cm<sup>2</sup>/hr. In inoculated flasks, the rate of corrosion of unprotected samples was 60 to 80% higher, and that of coated samples slightly lower than in the sterile medium. On stainless steel, V. desulfuricans developed well, reaching about 1.5 million cells/cm<sup>2</sup>, after 6 mo. The rate of corrosion was low (0.0007 to 0.001 gm/cm<sup>2</sup>/hr in sterile sea water), but was about 60% higher in the presence of bacteria.

236

Rozenberg, L. A., Korovin, Yu. M., Ulanovskii, I. B. EFFECT OF BACTERIA ON THE CORROSION OF STAINLESS STEELS. In: Marine Fouling and Borers, p. 252-261, 1968.

In Russian - Translated by National Science Foundation.

237

Rush, P. J. PRELIMINARY STUDIES CONCERNING STRUCTURES IN THE DEEP OCEAN. Naval Civil Engineering Lab. Technical Note No. N-447, AD-278 457: 14 p., June 27, 1962.

The bottom areas of deep oceans offer an entirely new environment for the use of structural materials. Except for signal cables, no man-made structures have been subject to long-term exposure to these conditions. Information about reactions of various materials under combinations

of high pressure, constant cold temperature, and immersion in salt water is scant. Available literature on corrosion in ocean waters has mostly to do with shallow depths where the problems of pressure, temperature, oxygen concentration and chemical elements are different from those to be expected in the very deep waters.

238

Satake, Jiro, Moroishi, Taishi, Nakajima, Takashi. THE EFFECT OF ALLOYING ELEMENTS ON SEA WATER CORROSION OF STEEL. I.- LABORATORY CORROSION TESTS. Corros. Eng. (Boshoku Gijutsu)., 18; No. 8: p. 19-24, August 1969.

In Japanese.

Four types of laboratory corrosion tests involving total or intermittent immersion in artificial sea water or tap water were carried out in order to study the effect of alloying elements on sea-water corrosion of Cu-bearing steel. The alloy compositions of 32 test steels varied with respect to C, Si, Mn, P, Cu, Ni, Cr, Ti and Al contents. Regression analysis was applied to the test results. Manganese, Ni, Ti and Al were found to have no effect on the corrosion. Carbon was harmful, while Cr and P, in some cases Cu and Si, were beneficial. Martensitic structure of 2% Cr steel was preferable to ferrite-pearlite structure as far as corrosion resistance to intermittent immersion in artificial sea water was concerned. Chromium content in the matrix appears to control the corrosion rate.

239

Schenk, Max. ALUMINUM AND WATER. Metalloberflache, 4: p. B33-B36, March, 1952.

In German

Corrosion of aluminum in natural waters occurs only in places on the metal surface where the natural oxide film has been damaged or where its growth is being prevented. Provided the contact with water is not too prolonged, a continuous, undamaged oxide film will protect aluminum against all types of natural water. Uninterrupted contact of aluminum with water or moisture leads to severe corrosion. Stagnant water is more dangerous than flowing water, and anodic oxidation gives little protection.

The aggressivity of fresh waters, including rain, snow, river water, and ground water, varies with their hard-

ness, oxygen content, and similar factors. Hard waters are less corrosive than soft waters.

Sea water is much more dangerous than fresh water. Aluminum exposed to sea water will corrode even after the metal is removed. The hygroscopic magnesium salts present in sea water prevent complete drying of the aluminum in air, so that the corrosive action continues after the metal is supposedly dry. Some aluminum alloys are more resistant to sea water than others. Anodizing can prolong the life of aluminum in sea water provided the water contains no heavy metal ions.

Among industrial waters, distilled water is the least harmful, but even this water can become dangerous for aluminum if it contains traces of metals such as copper and iron, which originate from tanks, armatures, pipes and pumps. Such water attacks aluminum even in the purest state, and anodic oxidation is ineffective. Tap water in continuous contact with copper pipes must be included in this category, even if it wets the aluminum only temporarily. Proper treatment of industrial waters is therefore mandatory.

240

Schlain, David, Kenahan, C. B. CORROSION RESISTANCE OF TITANIUM ALLOYS COMPARED WITH COMMERCIAL PURE TITANIUM. Corrosion, 14: p. 25-28, September 1958.

Titanium as well as its alloys with 8% manganese, 5% aluminum - 2-1/2% tin, 2% aluminum, 6% aluminum, 1% copper, and 5% copper are similar in chemical and galvanic properties. They are completely resistant to corrosion in synthetic ocean water, tap water, 1% sodium hydroxide, and 5% ferric chloride solutions. Contact with aluminum in synthetic ocean water or with magnesium in tap water does not affect this resistance.

241

Schreir, L. L., ed. CORROSION (2 VOL.). New York, John Wiley & Sons, 1963.

242

Schreitz, W. G. CORROSION-EROSION PROPERTIES OF 90/10 COPPER-NICKEL ALLOYS IN SEA WATER. Naval engineering Experiment Station. Report 4B(6)17XL603: 35 p., November 1951.

Results of sea water corrosion-erosion studies indicate that 90/10 copper-nickel alloy containing 1.0-1.75% iron, 0.75% manganese, and other constituents in accordance with ASIM B 111-49 is a suitable alternate as a sea water piping material

for the 70/30 copper-nickel alloy of Navy Spec. 44 T40a.

Laboratory type specimens 3/4 by 4 by 1/16 in. were tested by rotating them in sea water at 15 and 30 ft per sec. 90/10 Alloys with iron contents from 0.01 to 1.96% were compared with 70/30 alloys with both low and high iron contents. The corrosion rates of 90/10 alloys containing 1-2% iron were less than half the rate for low iron (0.05%) 70/30 copper-nickel, and it is concluded that for optimum corrosion-erosion resistance the 90/10 alloys should contain at least 1% iron. Heat treatment to put all the iron in solid form appears to enhance the behavior of the alloy. If the iron is not completely held in solution, however, no appreciable benefit is obtained from increasing the iron content above 1 or 1.25%.

Of three 90/10 copper-nickel piping branches assembled with bronze fitting of the silver brazing type, one with 1.5% iron which was operated for 9 mo at a sea water velocity of 9 ft per sec, behaved better than a similar system made up with 70/30 copper-nickel containing 0.05% iron and approached that of a high iron 70/30 alloy. Two branches of 90/10 piping operated for 6 mo at a water velocity of 15 ft per sec were in good condition when inspected.

Silver brazing did not appreciably change the magnetic permeability of the commercial 90/10 piping nor did it affect its corrosion resistance. There was no appreciable galvanic action between the pipe and the bronze fittings.

243

Schwartzlose, R. A., Sessions, M. H. EFFECT OF CORROSION, FISHBITES AND FOULING ON DEEP OCEAN MOORING MATERIALS. Proceedings, First Joint Aerospace and Marine Corrosion Technology Seminar. Held in Los Angeles, Calif., July 10-12, 1968.

244

Shal'nev, K. K. RESISTANCE OF METALS TO CAVITATION CORROSION IN FRESH WATER AND SEA WATER. Canada Defense Research Board, Defense Scientific Information Service. Translation T-153-R, AD 63515: 6 p., November 1954.

In Russian - Translation by E.R. Hope, from Doklady Akad. Nauk 95, 229-232, March 1954.

The resistance of brass, bronze, and gray cast iron to cavitation corrosion in fresh water and sea water was determined by the vibrator method using a magnetostriction apparatus. A sample of the test metal was fastened to the tip of the vibrator tube

which was driven at 8000 cycles per sec with an amplitude of 0.09 mm. The test pieces were immersed in boiled tap water or synthetic sea water at 25 C to a depth of 6 mm; the weight loss was determined after 90 min.

The hardness of the brasses and bronzes was a considerable factor in their resistance to cavitation corrosion; the composition of the water had little effect on the degree of attack. In contrast, the weight loss of gray cast iron in sea water was nearly twice as great as the weight lost in fresh water. The individual corrosion pits also were deeper in sea water than in fresh water.

A stagewise mechanism is postulated to explain the difference in cavitation corrosion observed in the gray cast iron in sea water and fresh water. The mechanism differs from mechanical and thermodynamic theories which state that the chemical composition of the water has no significance in the development of high pressures and temperatures produced in the collapse of cavitation hollows and which are considered the chief causes of cavitation corrosion.

245

Shcherbakov, P. S., Zobachev, Yu. Ye., Shuprun, L. A. CORROSION IN FLOWING SEA WATER. Sudostroyeniye, No. 6: p. 55-59, 1962.

In Russian

The Corrosion Laboratory of the Central Scientific Research Institute of the Maritime Fleet has conducted research on the corrosion of a number of steels and Cu, Al, and Mg alloys in flowing synthetic sea water. Temperature varied from 17 to 20 C and water speed from 2 to 16 m/sec, while exposure time was 250 hr. All materials showed higher corrosion rate as water speed increased. The corrosion rates were found to be 0.3 to 2.5 mm/yr. for carbon and low-alloy steels, 0.006 to 0.014 mm/yr. for stainless steels, 0.03 to 0.1 mm/yr. for Al-bronze, 0.03 to 0.26 mm/yr. for brass, and 0.03 to 0.59 mm/yr for M3 Cu (ASIM B72-55T). The dissolution rate of Mg and Al-base alloy protectors was found to be 1.0 to 30.0 mm/hr and was greatly accelerated by the presence of impurities (Fe, Cu, Ni).

246

Shcherbakov, P. S. EFFECT OF SODIUM NITRATE ON THE RATE OF CORROSION OF LOW-CARBON STEEL AT VARYING RATES OF MOTION OF THE LATTER IN SEA WATER. Zhur. Fiz. Khim., 36: p. 1360-1363, June 1962.

In Russian

The corrosion rates in flowing sea water of low-carbon steel, four low-alloy steels and gray iron were measured in a rotating disk apparatus. The disk carrying the samples was immersed in artificial sea water at 18 to 20 C and rotated at speeds from 2 to 16 m/sec for 250 hr. The water was changed every 50 hr. The samples were tested in water without additives and in the presence of varying concentrations of sodium nitrite.

At a nitrite concentration of 4, 2, and 1%, the rate of corrosion of low-carbon steel was less than 0.1 mm/yr and was practically independent of flow rate. At 0.35 and 0.1% concentrations, the rate was considerably higher and increased with flow rate, although more slowly than in water containing no nitrite. At higher inhibitor concentrations the rate in stationary sea water was 30 to 35% higher than in flowing water. No significant differences were observed between low-carbon steel and low-alloyed steels. Gray iron showed a higher rate, but the effects of sodium nitrite were essentially similar to its effects on steels.

To study the effects of sodium nitrite on the electrode processes, anodic and cathodic polarization curves of low-carbon steel were obtained at various sodium nitrite concentrations in stationary water and in water flowing at a rate of 2, 4, 12 and 16 m/sec. At 0.25% sodium nitrite, anodic polarization was weak and the potentials were more positive at lower flow rates. At 1 and 4% nitrite, an opposite phenomenon was observed: the potentials were shifted toward more positive values with increasing flow rate. Bubbling of oxygen through the sea water during anodic polarization shifted the potentials toward more positive values at all concentrations of the inhibitor. Cathodic polarization curves showed a rapid increase of potentials with increasing current density, but the limit diffusion current was practically the same at all concentrations of sodium nitrite and in its absence.

The reduction of the corrosion rate in flowing sea water, as compared with stationary water, in the presence of 1 to 4% sodium nitrite can be explained by assuming the participation of oxygen in the formation of the protective film on the metal surface. This assumption can also explain why in sea water the minimum protective concentration of sodium nitrite is many times greater than in fresh water. In sea water, the chloride ions are adsorbed on the metal surface, displacing oxygen, and thus interfering with protective film formation. Consequently,

complete passivation of the metal surface requires relatively large concentrations of sodium nitrite, and is facilitated by the presence of oxygen. The role of oxygen becomes particularly important at higher flow rates, when the protective film is exposed to mechanical damage. Under these conditions, restoration of the continuity of the film or its 'repair' is promoted in the presence of oxygen.

247

Southwell, C. R., Alexander, A. L., Forgeson, B. W., Mundt, H. W., Thompson, L. J. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 1. TEST METHODS USED AND RESULTS OBTAINED FOR PURE METALS AND A STRUCTURAL STEEL. Naval Research Lab., NRL Report 4929, June 1957.

248

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 2. ATMOSPHERIC CORROSION OF TEN STRUCTURAL STEELS. Naval Research Lab., NRL Report 5002, December 1957.

249

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 3. UNDERWATER CORROSION OF TEN STRUCTURAL STEELS. Naval Research Lab., NRL Report 5113, August 1958.

Eight year immersion studies of a modern controlled process (Aston) wrought iron were made in the tropical waters of Panama. The iron was most heavily corroded when continuously immersed in sea water. Weight losses in continuous fresh water immersion and at sea water mean tide were approximately equal. Pitting penetration was lowest at mean tide. At least 4 yr exposure was required to reach a condition of linear relationship between corrosion and time. The slopes of the curves at 8 yr suggest that for longer periods of exposure greater divergences can be expected, with sea water causing increasingly heavy corrosion, mean tide an intermediate amount, and fresh water relatively less.

Accelerated pitting penetration from exposure of samples with millscale surfaces is apparent only for continuous immersion in sea water. In this medium, millscale on wrought iron seems less harmful than steel millscale.

There is practically no difference between wrought iron and mild structural steel for the first 4 yr in both continuous sea and fresh water immersion. After 8 yr the wrought iron weight loss is significantly less than that for steel. At mean tide the wrought iron shows less corrosion damage at all periods of exposure.

When coupled together, wrought iron is anodic to steel in both sea and fresh water. However, a quantitatively signifi-

cant galvanic corrosion of wrought iron occurs only in continuous sea water immersion. Protection of steel by wrought iron requires a large area of wrought iron in relation to steel; under these conditions, the corrosion of steel is reduced by approximately one half.

In tropical atmospheric environments, wrought iron was much more heavily damaged by corrosion than any of the four proprietary low alloy steels tested.

250

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 2 - ATMOSPHERIC CORROSION OF STRUCTURAL STEELS. Corrosion, 14: No. 9: p. 55-59, September 1958.

251

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 4. WROUGHT IRON. Naval Research Lab. NRL Report 5370, AD-228 448: 15 p., October 1959.

252

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS, PART 5. STAINLESS STEELS. Naval Research Lab., NRL Report 5517, September 1960.

253

Southwell, C. R., Forgeson, B. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 4. WROUGHT IRON. Corrosion, 16: p. 120-126, October 1960.

The corrosion of Aston process wrought iron alone and galvanically coupled with mild structural steel was studied over an 8 yr period in five Panama Canal environments: continuous sea water immersion, mean tide immersion, continuous fresh water immersion, marine atmosphere and inland atmosphere. Comparison data on several structural steels exposed under the same conditions are given.

Continuous sea water immersion corroded wrought iron most heavily; weight losses in continuous fresh water and mean tide were approximately equal. Mean tide produced lowest pitting penetration. Slopes of curves at 8 yr exposure suggest greater divergence with increasing exposure time. Comparison of wrought iron and mild structural steel after 4 yr in continuous sea and fresh water showed practically no difference in the metals. After 8 yr, however, the wrought iron loss was significantly less than that of steel. At mean tide the wrought iron showed less corrosion damage at all periods of exposure. Even greater differences, in favor of the wrought iron, are probable for longer exposure periods.

Coupling tests showed that wrought iron is anodic to the steel in both sea and fresh waters. However, a quantitatively

significant galvanic corrosion of wrought iron occurred only for the continuous sea water immersion. Protection of steel by wrought iron requires a large area of the iron in relation to the steel, and under these conditions the corrosion of steel is reduced by approximately one half.

Millscale accelerates pitting only in continuous sea water. It was less harmful on wrought iron than on steel. After 8 yr in the marine atmosphere weight loss of wrought iron was 1.6 times greater than in the inland atmosphere. In both marine and inland atmosphere 8 yr weight losses of wrought iron were more than double that of any of four low alloy structural steels.

254

Southwell, C. R., Hummer, C. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 6. ALUMINUM AND MAGNESIUM. Naval Research Lab., Report No. NRL-6105, AD-609 618: 20 p., December 1964.

The corrosion resistance of three alloys of aluminum and two alloys of magnesium has been studied following exposure up to 16 years in five natural tropical environments. These include sea-water immersion, freshwater immersion, and exposure to tidal sea water, a tropical marine atmosphere, and a tropical inland atmosphere. Aluminum 1100, aluminum alloy 6061-T, and magnesium alloy AZ31X were exposed to each of the environments listed. In addition, alclad aluminum 2024-T and magnesium alloy AZ61X were exposed to the two tropical atmospheres. Weight loss, pitting, and change in tensile properties were measured to show the extent of corrosion for each of these materials. Aluminum alloys demonstrate extremely high resistance to each environment, with the exception of tropical fresh water, in which case serious pitting occurred. Alloy 6061-T demonstrated some superiority in all environments to aluminum 1100.

255

Southwell, C. R., Alexander, A. L., Hummer, C. W. CORROSION OF METALS IN TROPICAL ENVIRONMENTS - ALUMINUM AND MAGNESIUM. Materials Protection. 4: No. 12: 30-35, December 1965.

256

Southwell, C. R., Hummer, C. W., Alexander, A. L. CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 7. COPPER AND COPPER ALLOYS. SIXTEEN YEARS EXPOSURE. Naval Research Lab. Report No. NRL-6452, AD-644 930: 34 p., October 1966.

The corrosion of copper and nine wrought copper alloys is reported for exposures in five tropical environments for one, two, four, eight, and sixteen years. Weight loss, pitting, and change in tensile

strength were measured to evaluate corrosion resistance. Higher corrosion rates are shown for tropical sea water immersion and tropical marine atmosphere than similar exposures in temperate climates. Of the various alloys studied, 5% Al bronze showed the highest general corrosion resistance: its 16-year losses in sea water were only 1/5 that of copper. Copper and the high-copper alloys were resistant to all environments and generally had decreasing corrosion rates with time of exposure. Tensile tests revealed heavy dezincification in the lower-copper brasses when exposed in marine environments, and for two of the brasses in fresh water immersion. As a result of the decreasing corrosion rates or dezincification, anti-fouling properties of copper alloys decreased with time of exposure. All were moderately to heavily fouled after 16 years in sea water. Galvanic effects were pronounced in tropical sea water. The corrosion of copper alloys was accelerated appreciably by contact with stainless steel (316) of 1/7 their area, while similar carbon steel strips gave effective cathodic protection of plates of brass and bronze over the long term.

257

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 8. NICKEL AND NICKEL-COPPER ALLOYS - SIXTEEN YEARS' EXPOSURE. Naval Research Lab., Report No. NRL 6592, AD-661 835: 24 p., October 4, 1967.

Corrosion of nickel and nickel-copper alloys in five natural tropical environments is reported for exposure periods of 1, 2, 4, 8, and 16 years. Data collected include weight loss, pitting, change in tensile strength of simple plates, and weight loss of galvanic couples. Corrosion in the tropics is compared with available exposure results from temperate latitudes in the United States, and generally the tropical corrosion was appreciably higher. The weight-loss-vs-time curves are normally curvilinear relations but considerable variation in the direction and magnitude of the curvature was observed for the different metals and environments. With respect to pitting, the high nickel alloys developed severe early pitting under sea water. However, the initial high penetration rates leveled off to very low rates after the first 1 to 2 years' exposure. Comparison under tropical sea water of monel and copper-nickel with various other nonferrous metals shows copper-nickel with comparatively high corrosion resistance, but monel with the lowest sea-water resistance of the group. Galvanic corrosion results show the long-term efficiency of carbon steel anodes in cathodically protecting nickel-copper alloys in sea water. Ad-

ditional galvanic data reveal that considerable anodic corrosion can be induced in a normally sea-resistant metal if coupled with certain nickel alloys. The nickel metals were highly resistant to corrosion in the tropical atmospheres. There was no measurable pitting in these terrestrial exposures and only small weight losses. The losses that were measured though showed increasing resistance of the metals with increasing nickel content. Since tropical corrosion is near the upper limit of corrosiveness of natural environments, these long-term results should afford safe, practical information for design and protection of structures in all latitudes.

258

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN TROPICAL ENVIRONMENTS - COPPER AND WROUGHT COPPER ALLOYS. Materials Protection, 7: No. 1: 41-47, January 1968.

259

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN THE TROPICS: STRUCTURAL FERROUS METALS. In: National Association of Corrosion Engineers Twenty-fourth annual conference, 1968. Held in Cleveland, Ohio, March 18-22, 1968.

Reported is a study including history and summary of major metals revealing paucity of reliable long-term data in natural underwater environments. This study is one in a series describing results of long-term comprehensive corrosion investigation conducted in five local natural environments in the Canal Zone. Corrosion losses occurring in sea water, brackish water, fresh water, and mean tide are measured by weight loss, depth of pitting, and change in mechanical (tensile) properties. Data are included for a representative group of cast and wrought structural metals. Data from tropical environments are compared with that available from more temperate latitudes. Comparisons are made of different structural alloys over long periods of underwater exposure.

260

Southwell, C. R., Alexander, A. L.  
CORROSION OF STRUCTURAL FERROUS METALS IN TROPICAL ENVIRONMENTS - RESULTS OF 16 YEARS' EXPOSURE TO SEA WATER AND FRESH WATER. In: Proceedings, 24th. Conference, NACE, Sea Water Section. p. 685-695, 1969.

261

Southwell, C. R., Alexander, A. L. THE CORROSION OF METALS IN AQUEOUS ENVIRONMENTS OVER EXTENDED PERIODS. In: Third Inter-Naval Corrosion Conference, London, England. 1969.

262

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN TROPICAL ENVIRONMENTS - NICKEL AND NICKEL-COPPER ALLOYS. Materials Protection, 8: No. 3: 39-44, March 1969.

Corrosion data are reported for nickel and nickel-copper alloys exposed for 16 years to fresh water, sea water, sea water mean tide, and marine and inland atmospheres in the Panama Canal Zone. Major emphasis is on the sea water environments. Results reported include weight loss, pitting, and change in tensile strength for simple plates and weight loss for galvanic couples. Marine corrosion in the tropics is compared with available nickel alloy results from temperate latitudes in the United States. Time vs. weight loss and time vs. pitting curves are presented. A few other nonferrous metals are included for comparison.

263

Southwell, C. R. THE CORROSION RATES OF STRUCTURAL METALS IN SEA WATER, FRESH WATER, AND TROPICAL ATMOSPHERES. Corrosion Science, Great Britain, 9: p. 179-183, March 1969.

264

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN TROPICAL ENVIRONMENTS. PART 9. STRUCTURAL FERROUS METALS - SIXTEEN YEARS' EXPOSURE TO SEA AND FRESH WATER. Naval Research Lab. Report No. NRL-6862, AD-687 705: 32 p., April 1969.

Effects of corrosion on 20 structural ferrous metals immersed in seawater and fresh water and exposed at mean-tide elevation have been measured at various intervals during 16 years. Corrosion rates and time-corrosion curves derived from both weight loss and pitting have been established. The final constant rates provide significant data for comparing the corrosion resistance of the different metals in the various environments and for estimating service life over more extended periods.

265

Southwell, C. R., Alexander, A. L. MARINE CORROSION OF CAST AND WROUGHT NON-FERROUS METALS RESULTS OF SIXTEEN YEARS EXPOSURE IN THE TROPICS. In: Proceedings, Twenty-fifth Conference National Association of Corrosion Engineers. Held in Houston, Tex., March 10-14, 1969. p. 288-298, 1970.

A large mass of corrosion data from the waters and atmosphere of Panama has been collected as the result of a series of

studies initiated in 1947. Tropical exposures have the advantage of producing slightly higher corrosion rates than normally accrue from temperature latitudes, and therefore usually represent upper limit rates for corrosion in uncontaminated natural environments. These results, then, will contribute substantially in filling existing gaps in practical corrosion-rate knowledge. The major portion of the effort was directed toward evaluation of corrosion in marine environments. Fifty-two metals and alloys were selected for the 16-year study. Bimetallic couples as well as single plates were included. Over 13,000 individual specimens were exposed and a total of 168,000 data measurements made. This report will present the 16-year results for all wrought and cast non-ferrous metals exposed in three marine environments. Data from fresh water immersion are included for purposes of comparison.

266

Southwell, C. R., Alexander, A. L.  
CORROSION OF METALS IN TROPICAL WATERS: STRUCTURAL FERROUS METALS. Materials Protection, 9: No. 1: 14-22, January 1970.

Corrosion data are reported for 20 structural ferrous metals exposed up to 16 years in natural tropical waters, including sea water, fresh water and mean tide elevation. Time-corrosion curves derived from both weight loss and pitting are presented for many of the ferrous alloys and tabulated data for all metal environment combinations are included. These comprehensive long term results comprise the most extensive collection of accurate sea water and fresh water corrosion data presently available. After initial periods of changing slopes, corrosion rates for most of the ferrous metals stabilize to constant values. These steady state rates are presented for each exposure and provide a significant means for comparing the corrosion resistance of the different metals in the various environments and for estimating useful life over extended periods. Corrosion curves for eight low alloy steels, Aston process wrought iron, and various cast irons and steels are evaluated against C steel. Marine corrosion in the tropics is compared with available ferrous metal results from temperate latitudes.

267

Stewart, W. C., LaQue, F. L. CORROSION RESISTING CHARACTERISTICS OF IRON MODIFIED 90:10 CUPRO NICKEL ALLOY. Corrosion, 8: p. 259-277, August 1952.

Laboratory corrosion-erosion tests and service tests have demonstrated that, in installations where high resistance to corrosion and erosion by salt water is required, 90/10 cupronickel alloys with 1.5% or higher iron contents are equivalent to or superior to 70/30 cupronickel and similar alloys, such as Admiralty brass. They are reliable and economic substitutes for high-nickel alloys in condenser tubes and seawater piping systems, and are definitely superior where freedom from marine fouling organisms is also desired.

Cold-rolled strips of 88/12 cupronickel containing 1.8% iron, corroded at a rate of 0.0002 in. per yr, i.e., only one-third as fast as did a low-iron 70/30 cupronickel, when both were exposed for nearly 3 yr in slow-flowing seawater conducive to pitting and fouling. Similar, but shorter exposure of a 90/10 cupronickel containing 0.8% iron indicated that the iron content need not be as high as 1.8% to achieve good resistance to sea water, at least not under relatively quiet conditions. This alloy corroded without significant pitting at a rate of 0.0006 in. per yr, i.e., only one-sixth as fast as did similarly exposed arsenical Admiralty brass. Irrespective of their iron contents or heat treatments, a series of 90/10 alloys immersed in relatively quiet seawater remained substantially free from marine fouling, whereas the monel racks and fastenings showed heavy fouling attachments. Under these conditions, the freedom from fouling of the iron-modified 90/10 alloys is attributable to, and in agreement with their corrosion rates. These rates are sufficiently high to release copper in corrosion products at an average rate above 5 mg per sq dm per day - a value previously established as being required for a copper-containing surface to keep itself free from marine fouling organisms.

In high-velocity jet-impingement tests, 90/10 cupronickel containing 0.7 or 2% iron showed better resistance than Admiralty brass or low-iron 70/30 cupronickel. Its resistance was about equal or better than that of aluminum brass, and about equal to that of 70/30 cupronickel with high (0.5%) iron content. 90/10 Cupronickel containing 2 and 3.5% iron and quench annealed to hold the iron in solution performed better under jet impingement than did 90/10 alloys containing 0.8 and 1.5% iron.

Essentially identical conclusions were reached from erosion-corrosion tests on cupronickel samples mounted on a rotating

disc, and on disc specimens mounted on a rotating spindle. Resistance increased with increasing iron content. The higher the speed of rotation, the higher the iron content required to confer protection against attack. Even when heat-treated to precipitate a maximum amount of iron, the 90/10 alloys were still superior to 70/30 cupronickels and to Admiralty brass. With 3.5% iron content, quench-annealing to hold the iron in solution was necessary for best erosion-corrosion resistance.

268

Stover, H. E. PREMATURE FAILURE OF COPPER-NICKEL ALLOYS IN SEA WATER. Corrosion, 17: p. 83-84, October 1961.

Monel and 90/10 copper-nickel bands used to tie plastics film around creosoted wooden pilings for protection against marine borer attack failed from extreme corrosion after 1 yr in salt water (Port of Los Angeles) despite the far greater expected service life of the alloys in this environment. Corrosion seemed to be greatest near the mudline. The black corrosion product on both metals was a mixture of sulfides and alloyed metals; both metals became somewhat magnetic. Several possible theories to explain these premature failures are advanced.

269

Summerson, T. J., Pryor, M. J., Keir, D. S., Hogan, R. J. PIT DEPTH MEASUREMENTS AS A MEANS OF EVALUATING THE CORROSION RESISTANCE OF ALUMINUM IN SEA WATER. Am. Soc. Testing Materials, Spec. Tech. Publ. No. 196: p. 157-175, November 1957.

This method is based on a statistical treatment of penetrometer measurements of every pit present on test specimens of aluminum immersed in sea water for periods up to 24 mo. The best approximation to normal frequency distribution curves is obtained by plotting the square root of the pit depth against the frequency of pitting. Calculations of the mean square root pit depth, the standard deviation, and standard error of the mean square root pit depth are shown. The importance of the mean square root pit depth, the standard deviation, and the frequency of pitting in determining the manner by which pitting corrosion proceeds is discussed.

A sampling procedure is suggested whereby quantitative data on the resistance of aluminum to pitting corrosion in sea water can be determined at arbitrarily chosen confidence limits by measuring only a fraction of the total number of pits present.

270

Sutton, Frank. EVALUATION OF TITANIUM AS A SALT WATER PIPING MATERIAL. Naval Engineering Experiment Station. Evaluation Report 910037D, AD-212 792: 8 p., September 1958.

An experimental piping system was constructed of 75A titanium tubing of 1-1/4 in. outside diameter by 1/16 in. wall thickness. Valves and fittings were of cast titanium; joints were welded in a helium atmosphere.

After handling sea water for 39 mo at an average velocity of 20 fps, the system showed no signs of erosion or corrosion. Bronze valves which were included for 11 mo of the run showed moderate body corrosion and erosion; their Monel seats and discs were roughened slightly. The run was too short to evaluate galvanic corrosion of the bronze.

Because of its high cost and difficult working, titanium piping is recommended for use only at velocities too high for copper-nickel systems.

271

Tavadze, F. N., Mandzhgaladze, S. N. CORROSION RESISTANCE OF TITANIUM ALLOYS. Naval Intelligence Command, Translation Div. AD-715,254: 6 p., November 19, 1970.

Translation from Korroziionnava Stoikost Titanovykh Splavov, Moscow, 1969, p.177-182.

Titanium has good resistance to corrosion in sea water, has high strength, and a low specific weight, so has wide-ranging future prospects for use in shipbuilding. Titanium is very widely used as a shipbuilding material.

272

Taylor, Edward. EVALUATION OF METALLIC MATERIALS EXPOSED TO THE DEEP OCEAN ENVIRONMENT AT 5640 FEET FOR 123 DAYS. Naval Air Engineering Center. Report No. NAEC-AML-2132, AD-466 955: June 1965.

Over 200 metallic specimens of 30 different compositions attached to submersible test unit 1-3 exposed to the deep ocean environment at 5640 ft. approximately 31 nautical miles west of Port Hueneme, California, for a period of days have been evaluated for deteriorative effects. Specimens were exposed in the following conditions: (A) heat treated; (B) welded; (C) painted; (D) stressed; and (E) coupled. Corrosion rates were calculated for those metals exhibiting uniform general attack such as the alloy steels, stainless steels and copper base alloys. Those metals under-

going selective corrosion such as pitting of certain aluminum alloys were evaluated for the frequency and severity of attack. Certain high strength steels and stainless steels exposed at stress levels below their yield strengths were metallographically examined for evidences of microstructural attack and/or stress corrosion cracking. No evidence of either phenomenon were found in the specimens in question. Severe macroscopic crater type pitting was disclosed in 5456-H34 aluminum alloy. An increase, over shallow depth exposures, in the severity of intergranular attack and exfoliation attack is noted in the appropriately susceptible tempers of the 2000 and 7000 series aluminum alloys, in both the welded and non-welded conditions.

273

Taylor, E. CORROSION RESISTANCE OF MULTIPHASE ALLOYS. Materials Protection, 9: No. 3: p. 29-31, March 1970.

According to the author, Multiphase Alloy MP35N is virtually immune to seawater attack, is highly resistant to corrosion in a wide range of chemical environments, is not susceptible to stress corrosion cracking by hot or cold chlorides, and is not embrittled by hydrogen. Its ultra high strength and excellent fatigue properties make it applicable in the hydrospace and aerospace industries.

274

Teraï, Shiro, Baba, Yoshio. EFFECT OF SURFACE TREATMENTS ON THE CORROSION OF ALUMINUM AND ITS ALLOYS IN CONTACT WITH OTHER METALS IN ARTIFICIAL SEA WATER. Sumitomo Light Metal Tech. Rept., 3: p. 9-17, January 1962.

In Japanese with English summary

The effects of painting and of chemical conversion and electrochemical treatments on the corrosion of aluminum and its alloys in contact with other metals were studied in artificial sea water (6% NaCl + 0.3% H<sub>2</sub>O<sub>2</sub>) for periods ≤ 15 days.

Carbon steel, copper and silver in contact with aluminum or its alloys caused similar rapid and severe corrosion; stainless steel and titanium caused pronounced corrosion. Zinc or tin-plated steel did not greatly increase corrosion.

With 99.99% aluminum, pitting was severe and concentrated at the junctions; with 99.2% (Commercial purity) aluminum, corrosion was more distributed, with remarkably greater weight losses. With or without surface treatment, pit depth in 5052 alloy (2.29 Mg, 0.27 Cr, 0.28 Fe)

was less than in 99.2% aluminum or 3003 alloy (1.16 Mn, 0.45 Fe). There was no detectable weight loss of 2117 (2.65% Cu, 0.32% Fe) in contact with other metals.

Contact corrosion of aluminum and its alloys protected by Boshmite, ammonia, MBV or Alodine treatment was about half that after chemical polishing or non-treatment. With sulfuric or oxalic acid anodizing, contact corrosion was less than after chemical conversion treatments, but some pits about 0.2 mm deep occurred at the junctions with other metals. Zinc chromate primer or vinyl coating gave the best protection to aluminum in contact with other metals.

275

Thompson, J. C., Logan, R. K., Nehrich, R. B. A SURVEY OF MATERIALS RESEARCH IN OCEAN ENVIRONMENTS. Navy Electronics Lab. NEL Report 1110: 44 p., July 31, 1962.

276

Thompson, J.C. Logan, R. K. EFFECTS OF DEEP- AND SHALLOW-OCEAN ENVIRONMENTS ON CONSTRUCTION MATERIALS. Naval Electronics Lab. Center. Report No. NELC-1593, AD-848 079: 20 p., November 1968.

277

Tomashov, N. D. CORROSION AND PROTECTION OF METALS IN SEA WATER. Akademiia Nauk SSSR, Institut Fizicheskoi Khimii, Trudy, No. 8, Issledovaniia PO Korrozii Metallov, No. 6: p. 313-332, 1960.

278

Tomashov, N. D. THEORY OF CORROSION AND PROTECTION OF METALS. p. 454-481, New York, The MacMillan Company, 1966.

Trans. and Edited by B. H. Tytell, I. Geld, and H. S. Preiser.

279

Tracy, A. W., Hungerford, R. L. THE EFFECT OF THE IRON CONTENT OF CUPRO-NICKEL ON ITS CORROSION RESISTANCE IN "SEA WATER". Proc. Am. Soc. Testing Materials. 45: p. 591-617, 1945.

The beneficial effect of iron additions on the corrosion resistance of cupro-nickel alloys exposed to a 3% solution of sea salt in motion was investigated. Sheet metal specimens were attached to fiber disks rotated in the test solution; tube specimens were placed in an experimental condenser.

For sheet metal specimens, the extent of corrosion was determined by measuring losses in thickness with sharp-pointed micrometers. Corrosion of the tube specimens was judged by visual examinations.

The greatest improvement in resistance was imparted to cupro-nickels which had between 10 and 20% nickel. The addition of iron improved the alloy with 5% nickel to a fair degree and the alloy with 2% nickel somewhat. Approximately 1% iron had no effect in increasing the resistance of copper to "sea water" impingement corrosion. As the nickel content of cupro-nickels decreased from 30 to 5%, more iron was required for optimum corrosion resistance. For example 0.5% iron was required for the 30% cupro-nickel, 0.6% for the 20%, 0.75% for the 10% and 1% for the 5% alloy.

There was no indication in these tests that a critical relationship between the iron and manganese content of cupro-nickels affected corrosion resistance.

The data tend to confirm statements in the literature that 30% cupro-nickel builds a more protective film in sea water that is thoroughly aerated than in sea water deficient in air. This may be the basis of the better service understood to be obtained from 30% cupro-nickel in ships, where the velocity and turbulence of the sea water is greater than in central power stations, where the oxygen content may be low due to pollution of harbor waters.

280

Tuthill, A. H., Schillmoller, C. M. GUIDELINES FOR SELECTION OF MARINE MATERIALS. Paper presented at the Ocean Science and Ocean Engineering Conference, Washington, D. C., Marine Technology Society, June 1965.

281

Tuthill, A. H. MARINE CORROSION. Mach Design, 40: No. 30: 117-122, December 19, 1968.

Design and material selection for combating galvanic and crevice corrosion and stress-corrosion cracking in structures exposed to sea water are discussed. Reviews the effects of water turbulence and depth, and water or equipment velocity on corrosion and failure. Data are presented for a variety of ferrous and nonferrous materials on corrosion potentials in flowing (8-13 fps) sea water at 50 to 80 F., galvanic relationships for fastener, pump and valve materials and the fouling resistance of materials in sea water.

282

Tuthill, A. H., Schillmoller, C. M. GUIDELINES FOR SELECTION OF MARINE MATERIALS. Nav. Eng. J., 81: No. 2: 66-89, April 1969.

Users and designers of marine equipment have available a large backlog of published data and experience for the selection of economical materials that will give reliable and durable service. Charts and summaries of these data are presented that permit the designer to screen his initial materials selection in terms of general wasting away, pitting, crevice effects, fouling, velocity effects and cavitation, galvanic effects, selective attack, stress corrosion cracking, deep immersion, and cost. These principles are applied in the selection of materials for sea water heat exchange systems, propellers, stern tube bearings, marine hardware, fasteners, marine wire rope, buoys, and floating platforms. Materials considered are Ni-Cr-Mo alloys, Ti, 304, 316, and 400 steels, Ni-Cr alloys, Ni-Cu alloys, Ni, 70/30 Cu-Ni, 90/10 Cu-Ni, Cu, admiralty, Al brass, bronzes, Zn, Al, C steel, cast iron, austenitic Ni cast iron, etc.

283

Uhlig, H. H. BEHAVIOR OF NICKEL-COPPER ALLOYS IN SEA WATER. Record Chem. Progress. 7: p. 56-57, 1946.

Nickel copper alloys below 40% nickel are apparently in the active state and release sufficient copper ions in sea water to discourage fouling. Above 40% nickel, the alloys are passive; in this state corrosion of the general surface (not the pits) is insufficient to release a toxic minimum of copper. The appearance of corrosion pits is due to the action of passive-active cells. At this percentage composition it seems that the alloys should transform from the active to the passive state or the reverse.

Nickel is characteristically subject to biological fouling in sea water and corrodes in localized areas called pits. This form of corrosion depends on the electrolytic action of so-called passive-active cells and occurs in many passive metals, including chromium and the stainless steels. Passivity is that state in which a metal, normally active according to the EMF series, exhibits the electrochemical behavior of a more noble metal.

Copper, unlike nickel, does not foul in sea water and corrodes uniformly. The corrosion rate as measured by weight loss of metal is somewhat higher for copper than for nickel.

284

Uhlig, H. H., ed. CORROSION HANDBOOK. New York, John Wiley & Sons, 1948.

285

Uhlig, H. H. CORROSION AND CORROSION CONTROL, New York, John Wiley & Sons, 1963.

286

Ulanovskii, I. B., Nikitina, N. S. THE INFLUENCE OF PUTRIFYING AEROBIC BACTERIA ON THE CORROSION OF STEEL IN SEA WATER. Mikrobiologiya, 25: p. 66-71, January-February 1956.

In Russian with English Summary

Intensification of corrosion of steel in sea water containing putrifying bacteria is due to differential aeration and a decrease in pH values of sea water close to the steel surface where bacteria concentrate.

Tests were carried out using bacteria isolated from sea water and from corrosion products on steel in sea water. Sheet steel panels (100 x 50 x 1 mm) were cleaned, immersed for 15 min in 2 day old cultures of the bacteria, then suspended in sterile sea water at 15 to 18 C. Water was changed weekly. The bacteria isolated from corrosion products were more aggressive than those isolated from sea water. Thus, after 6 mo exposure the corrosion rate for steel exposed to bacteria isolated from corrosion products was 0.0379 g per sq m per hr, while for steel exposed to bacteria from sea water the rate was 0.0366. For a sterile, noninoculated surface similarly exposed, the rate was 0.0296 g per sq m per hr, or roughly 20 to 25% less than when bacteria were present.

The corrosion rate after only 2 wk of test was 0.0637 g per sq m per hr for bacteria-inoculated panels and 0.0469 g for sterile sheets. In the following 2 mo the rate of corrosion decreased rapidly. The number of bacteria at the start of the test was 3500 per sq cm of steel surface; after 30 days it was 1,660,000.

287

Ulanovskii, I. B., Korovin, Yu. M. CORROSION OF STAINLESS STEEL AT CONTACTS WITH NON-METALLIC MATERIALS. Zhur. Priklad. Khim. 31: p. 1366-1370, September 1958.

In Russian

Three types of stainless steels were placed in contact with rubber, plexiglas, or textolite and exposed to sea water at 15 to 16 C. Corrosion at the contact was attributed not only to galvanic effects, but to a stagnant zone between the

electrodes and to chlorine ions.

Data were plotted showing that current intensity, and hence corrosion, increased with cathode size. With anode areas of 0.8 sq cm, weight losses after 24 hr were 2.2, 1.0, 0.8, 0.6, and 0.4 mg at cathode areas of 540, 270, 145, 80 and 45 sq cm, respectively.

The influence of pH on the electric potential of steel in sea water was studied by adding hydrochloric acid. At low pH, the electrode potential shifted to the negative; at pH 4 this shift was especially marked. The pH decreased from 8.4 to 2 as anode current density increased from 0 to 0.2 ma per sq cm over a 24 hr period. The pH decreased from 8.4 to 3.9 with continued anode polarization for 25 hr at a current density of 0.012 ma per sq cm. The electrical potential of steel changed from -0.25 to -0.75 v at pH 5.5 and from 1.75 to -0.5 v at pH 4.3. The potential was stable at pH 2.3 and 3.0.

Peripheral corrosion of samples was observed at the contact gap after 120 hr in Black Sea water in 6- and 20-liter vessels. After 240 hr, corrosion covered 50% of the contact surface; after 360 hr, complete corrosion was observed. The onset of corrosion led to the formation of metal chloride solutions and to increases in pH as a result of the lowered electrode potential of the entire contact surface. Corrosion at the contact gap increased as the metal potential shifted to more negative values and the pH decreased below 5.5. In extended tests, the water in the vessels was changed every 48 hrs to assimilate natural conditions.

288

Ulanovskii, I. B. CORROSION OF ALUMINUM AND ITS ALLOYS IN SEA-WATER. *Zashchita Metallurgii*, 2: No. 4: 462-466, 1966.

In Russian

The corrosion of Al and several typical commercial Al alloys in sea-water was studied. On increasing pH of sea-water, stationary potentials of Al and its alloys begin moving in negative direction, even a change from pH 8 to 8.5 producing a shift of several hundred mV. This has a substantial effect on corrosion processes. Owing to reduction of O on Al, medium becomes more alkaline in cathodic regions, and potentials of these regions gradually becomes more negative; corrosion-pair current thus falls.

289

Ulanovskii, I. B., Turpaeva, E. P., Simkina, R. G., Korovin, Yu. M. EFFECT OF THE MUSSEL MYTILUS GALLO-PROVINCIALIS L. ON STEEL CORROSION. *Marine Fouling and Borers*, p. 246-251, 1968.

Translated by Mercado, A National Science Foundation, Special Foreign Currency, Science Information Program.

290

Upton, B. CORROSION RESISTANCE IN SEA WATER OF MEDIUM STRENGTH ALUMINUM BRONZES. *Corrosion*, 19: p. 204t-209t, June 1963.

Corrosion behavior of medium strength 90-10 aluminum bronzes of the BS 2032 type in sea water is markedly affected by the microstructural constituents present and their form. Resistance is good in the absence of gamma<sub>2</sub> in a continuous form. Factors influencing gamma<sub>2</sub> formation are cooling rate from the alpha + beta region and chemical composition. Beta phase retention, hence good corrosion resistance, is favored by a rapid cooling rate and high manganese content; nickel also favors beta retention, but it is much less potent than manganese. The effect of iron is variable and depends on the aluminum content. In the absence of alloying elements, beta breakdown is sensitive to aluminum content; it is faster at a high aluminum content. Silicon addition gives rise to a close-packed hexagonal kappa phase not easily decomposed to alpha + gamma<sub>2</sub>. This insensitivity to cooling rate, coupled with satisfactory mechanical properties and corrosion resistance, could provide a basis for design of an alternative alloy to B.S. 2032. A tentative specification is 6.0 to 6.4% aluminum, 2.0 to 2.4% silicon, 0.8 to 1.0% iron with the balance copper.

291

Upton, B. BRAZING ALLOYS FOR MARINE SERVICE. *British Corrosion Journal*, 1: No. 4: 134-137, 1966.

Microstructure of brazing alloys to B.S. 1845 and to certain proprietary specifications is reviewed and related to corrosion performance in sea water on joints with copper, 70/30 cupro-nickel and 7% aluminium bronze. Factors influencing corrosion are illustrated and discussed and recommendations are made as to suitability of various braze metal-parent metal combinations. Of seven brazing alloys tested with three parent materials, only two were completely satisfactory, two could be used within certain limitations and three were unsatisfactory.

292

Uusitalo, Eino, Makimattila, Iikka.  
THE SEA WATER CORROSION OF SHIPBUILDING  
PLATES. Teknillisen Kemian Aikakauslehti,  
18: p. 513-517, 1961.

In Finnish with English summary

Study of the effects of temperature, salt level, rate of flow and attack duration on the corrosion rate of ship plates shows differences  $\leq 10\%$  between 10 different types of plate. Corrosion rates follow a parabolic law in relation to the duration of attack and the flow rate. Corrosion increases between 0 and 50 C; the effect of salt content ( $\sim 2\%$ ) is greatest at 25 C. There is no fundamental difference between the corrosion rates of killed and rimmed plates. Corrosion resistance increases with increase in copper, nickel, chromium, and arsenic contents. Increase in carbon content seems to improve the resistance of killed plates and to lower that of rimmed plates. Differences in corrosion rates of different types of plate are much greater when the plates are connected under various conditions.

293

Uusitalo, E. GALVANIC CORROSION OF STEEL  
PLATES AND WELD METALS OF HULLS IN SEA  
WATER. In: Proceedings, 2nd. Inter-  
national Congress on Metallic Corrosion,  
New York, N.Y., March 11-15, 1963.  
p. 812-814, 1963.

294

Uusitalo, Eino. EFFECT OF FLOW RATE ON THE  
GALVANIC CORROSION OF LOW-CARBON STEELS  
IN SEA WATER. Corrosion, 17: p. 89-92,  
February 1961.

The effect of flow rates ranging from 0 to 5 m/sec on the galvanic corrosion of eight low carbon steels in sea water at 0 C was studied by recording current-potential curves of the steel and by measuring the potentials, current strengths and weight losses of galvanic cells formed by coupled steels.

The corrosion of coupled steels was up to 15 times greater at high rates of flow than in still water, but variation of flow rate did not alter the order of nobility of the steels. The higher the silicon content of the specimens (which included weld metals and ship plates), the lower the nobility - composition being otherwise similar.

295

Vaders, E. CORROSION, PARTICULARLY OF  
COPPER-ZINC-ALLOYS, FROM SEAWATER AND  
CHEMICAL SOLUTIONS, PART II. Metall,

16: p. 1210-1224, December 1962.

In German

A large number of experimental copper alloys, especially copper-zinc alloys in sheet form, were evaluated for their resistance to artificial sea water, 10% sulfuric and acetic acids, 10% potassium and ammonium hydroxides and a sulfite solution. Alternate immersion tests in sea water were continued for 180 days. Weight losses in  $gm/m^2/day$  were determined.

Generally good agreement was observed between laboratory results and service performance. In synthetic sea water, zinc-free copper alloys as a group behaved worse than zinc-containing alloys. Aluminum, nickel and iron improved the resistance of zinc-free copper alloys; silicon and lead impaired their resistance against all corrosive media, except sulfurous acid (sulfite cooking liquor). DIN alloy 1714 showed the lowest weight loss among zinc-free compositions; this is in agreement with the known service performance of this alloy. Among zinc-containing copper alloys, as among all alloys examined, the aluminum-containing composition was by far the best. Manganese and lead improved or impaired the resistance of copper-zinc alloys, depending on alloy composition. High amounts of manganese or silicon reduced resistance of both zinc-containing and zinc-free alloys. Additions of nickel appeared to be beneficial up to  $\sim 10\%$ ; higher proportions often impaired resistance. This agrees with the observation that high-nickel alloys often do not perform according to expectations in sea water. In alternate immersion tests, copper-zinc alloys containing additions of aluminum with or without manganese gave the best performance; aluminum-free alloys were inferior. In flowing sea water, which was more corrosive than stagnant sea water, zinc-containing alloys were expectedly superior to zinc-free alloys; additions of manganese showed a detrimental effect, especially in higher proportions. High amounts of nickel improved resistance to flowing sea water, whereas additions of aluminum were less effective than in the static immersion test. In general, no significant differences were observed between annealed and unannealed specimens, although some unannealed (rolled or cast) specimens were more resistant to corrosion than the corresponding annealed alloys.

296

Vind, H. P., Noonan, M. J. BIOLOGICAL  
CORROSION AT NAVAL SHORE FACILITIES  
(WITH APPENDED BIBLIOGRAPHY ON BIOLOGICAL  
CORROSION). Naval Civil Engineering Lab.

Report No. NCEL-TN-831, AD-684 423:  
93 p., July 1966.

Bacteria and other organisms frequently initiate or accelerate corrosion of metals. Experiments were undertaken to ascertain if the presence of microorganisms is necessary for corrosion to occur. In aerated sea water, iron corrodes fairly rapidly whether or not microorganisms are present; but in sea water, from which oxygen is excluded, iron rusts very slowly unless sulfate-reducing bacteria or their metabolic by-product, hydrogen sulfide, is present. To induce rapid anaerobic corrosion, the bacteria must be supplied with carbohydrates or other nutrients. Anaerobic conditions and bacterial nutrients might both be found in the layer of slime that accumulates on the surfaces of structures placed in the ocean.

297

Von Fraunhofer, J. A. LEAD CORROSION IN SEA-WATER. Anti-corros. Methods Mater., 16: p. 21-24, 26-27, May 1969.

Study of the corrosion of lead in sea water and saline solution and of the anodic behavior of lead in chloride solutions was carried to give information applicable to the use of submerged telecommunications cables and the growing use of lead anodes for cathodic protection of marine structures. Review of previous work (39 references) on corrosion of lead in chloride solutions, effect of oxygen on rate of lead corrosion, corrosion rate of lead in sea water, and mechanism and rate of corrosion of lead alloys (lead with silver, cobalt, thallium, platinum, and tin), is presented. Although the corrosion resistance of lead and lead alloys in sea-water favors its wide use, there is still insufficient knowledge available on the nature of the corrosion product that is formed upon the metal and the role played by the metals used in the alloys.

298

Vreeland, D. C. ANODIC SEA-WATER CORROSION OF COMPOSITE METALLIC MATERIALS FOR MECHANICAL SHAFT SEALS. Naval Ship Research and Development Center. Report NSRDC 2479, AD-828 192L: 37 p., February 1968.

299

Vreeland, D. C. GALVANIC CORROSION BEHAVIOR OF WEAR-RESISTANT MATERIALS FOR MECHANICAL SHAFT SEALS. Navy Marine Engineering Lab. Report No. MEL-242/66, AD-635 592: 15 p., July 1966.

Shaft seals currently used on submarines employ mating wear surfaces which are supported by monel carrier rings. Galvanic corrosion effects between various candidate mating materials and monel have been investigated by the exposure of couples in seawater. The 14 materials exposed included seven cobalt-chromium alloys, six sintered carbide materials, and one copper-lead-tin alloy. The results indicate that galvanic coupling to monel had no adverse effect on the corrosion behavior of five of the cobalt-chromium alloys, and one of the sintered carbide materials.

300

Vulfson, V. I. CORROSION EXPERIMENTS ON METALS IN SEA WATER. Akademia Nauk SSSR. Komissia PO Bor'be S Korroziei Metallov, Trudy, No. 1; p. 44-57, 1951.

301

Wacker, G. A. STRESS-CORROSION STUDIES OF ALUMINUM ALLOY 7079-T6 IN SEAWATER. Navy Marine Engineering Lab. Report No. MEL-444/65, AD-626 374: 22 p., January 1966.

The stress-corrosion susceptibility of aluminum alloy 7079 in the T6 temper was investigated as a function of longitudinal, long-transverse, and short-transverse plate orientations. The alloy was found to be susceptible to stress-corrosion and pitting attack. Specimens oriented in the short transverse direction had the lowest resistance to damage in seawater. Variations in orientation-dependent stress-corrosion cracking susceptibility were related to microstructural characteristics. The alloy is considered unsuitable for Naval applications under conditions conducive to stress corrosion.

302

Wacker, G. A. STRESS-CORROSION STUDIES OF ALUMINUM ALLOY 5456-H321 IN SEAWATER. Naval Ship Research and Development Center. Report No. NSRDC 2436, AD-656 573: 27 p., July 1967.

The stress-corrosion susceptibility of aluminum alloy 5456 in the H321 temper was investigated as a function of longitudinal, long transverse, and short transverse plate orientations. The alloy was found to be subject to pitting attack but immune to stress-corrosion cracking in flowing seawater at ambient temperature.

303

Wacker, G. A. EFFECTS OF MARINE ENVIRONMENT ON HIGH-STRENGTH STEELS.

In: Materials Performance and the Deep Sea, p. 68-87, 1969.

Summarizes the general and stress-corrosion cracking behavior of several classes of high-strength steels in the marine environment. Eleven experimental heats of maraging steel were evaluated for resistance to stress-corrosion cracking in sea water. Those alloys containing 10 and 12% Ni were found to be susceptible to pitting attack and stress-corrosion cracking, while 18% Ni maraging steels were found to be highly resistant to pitting attack. The corrosion characteristics of 5Ni-Cr-Mo-V HY-130 steel were also investigated in natural sea water. The stress corrosion threshold stress for HY-130 was determined utilizing the criteria of no failure for six months of exposure in natural sea water under sustained stress in the precracked cantilever test. A major portion of the investigative work was concentrated on answering the question of whether long-term continuous cathodic protection of HY-130 in natural sea water will lead to eventual problems associated with H<sub>2</sub> embrittlement. The effect of cathodic protection on the low-cycle corrosion fatigue behavior of HY-130 was also determined.

304

Waldron, L. J., Peterson, M. H., Forgeson, R. W. ABYSSAL CORROSION AND ITS MITIGATION. PT. I, DETAILS OF PILOT TEST EXPOSURE. Naval Research Lab., NRL Memorandum Report 1282: March 1962.

305

Waldron, L. J., Forgeson, B. W., Peterson, M. H., Brown, B. F. ABYSSAL CORROSION AND ITS MITIGATION. PT. II. RESULTS OF A PILOT TEST EXPOSURE. Naval Research Lab., NRL Memorandum Report 1383. December 1962.

306

Waldron, L. J., Forgeson, B. W., Peterson, M. H., Brown, B. F. ABYSSAL CORROSION AND ITS MITIGATION. PT. III. RESULTS OF EXPOSURES ON DEEP SEA BUOYS OF THE WOODS HOLE OCEANOGRAPHIC INSTITUTE (EXPERIMENTS T-IV AND T-V.) Naval Research Lab., NRL Memorandum Report 1377: January 1963.

307

Waldron, L. J., Forgeson, B. W., Peterson, M. H., Brown, B. F. PERFORMANCE OF STAINLESS STEEL GALVANICALLY COUPLED TO OTHER METALS. Naval Research Lab., NRL Memorandum Report 1388: AD-679 659: 12 p., January 1963.

The report presents the results of exposing specimens of AISI type 316 stainless

steel, provided with standard crevices, and galvanically coupled with various other metals, in sea water. The exposure lasted 115 days. Complete protection against all forms of corrosion (including crevice corrosion) was afforded the 316 steel by coupling with most of the metals, including the standard aluminum-base and zinc-base galvanic anodes. No evaluation of the effectiveness of magnesium alloys could be made because the anode was completely expended before termination of the experiment. AISI type 316 L was observed to crevice-corrode when coupled to the regular 316, and in that instance the 316 did not crevice-corrode.

308

Waldron, L. J., Peterson, M. H., Brown, B. F. PRELIMINARY EXPERIMENTS ON DEEP SEA CORROSION AND CORROSION PREVENTION. Naval Research Lab., NRL Memorandum Report 1242: AD-693 119: 12 p., 1969.

Panels of mild steel were exposed in constant immersion near the surface of the ocean at Chincoteague, Virginia, and at 3100 feet in the sea near the Bahama Islands. Similar panels coupled to aluminum-zinc galvanic anodes of commercial composition and panels of AISI type 304 stainless steel were similarly exposed. The results of these short-term tests (two months) indicated that (1) mild steel corroded much faster at the deeply submerged location than at the surface, (2) galvanic anodes were fully effective in preventing corrosion at the deep location, but the current demands appeared to be more severe than near the surface, and (3) the stainless steel panel at Chincoteague suffered severe crevice corrosion, but the one in the deep site was totally unattacked.

309

Watkins, L. L. CORROSION AND PROTECTION OF STEEL PILING IN SEAWATER. Army Coastal Engineering Research Center. Report No. TM-27, AD-690 803: 108 p., May 1969.

The report, based on a survey of literature, assembles much of the current knowledge concerning corrosion and protection of steel piling in seawater. Causes of corrosion and effects of environmental conditions are presented. Results of tests on protective coatings for steel are included. Corrosion rates of bare steel piles and the factors involved in the use of cathodic protection and concrete jackets are explained. References surveyed show that flame-sprayed zinc sealed with vinyl is possibly the

best coating system tested. More data is needed from which to determine the most economical method of protecting steel piling in seawater.

310

Wesley, W. A. TOTAL IMMERSION TESTS. In: Corrosion Handbook, Uhlig, H. H., Ed., p. 959-965, New York, Wiley, 1948.

311

Wheatfall, W. L. METAL CORROSION IN DEEP-OCEAN ENVIRONMENTS. Navy Marine Engineering Lab. Report No. MEL-429/66, AD-645 481: 31 p., January 1967.

Experiments were conducted in deep-ocean environments to determine whether unusual corrosion phenomena exist at great depths that are not present in water near the surface. A total of five exposures were made at various locations in the Pacific Ocean. Two exposures were at 5640 feet, and one each at 2340, 5300, and 6780 feet. In some cases, similar tests were conducted in shallow water. Results from general corrosion tests of metals representing six typical alloy classes, and also from crevice-corrosion tests on a stainless steel and nickel alloy, revealed that, in general, there were no major differences between corrosion phenomena in deep-ocean and shallow-water environments. Variations in behavioral patterns that were observed could largely be explained on the basis of differences in oxygen content.

312

Wheatfall, W. L. METAL CORROSION IN DEEP-OCEAN ENVIRONMENTS. Naval Engineers Journal, 79: No. 4: 611-618, August 1967.

313

Williams, W. L. ALUMINUM BRONZES FOR MARINE APPLICATIONS. J. Am. Soc. Naval Engrs., 69: p. 453-461, August 1957.

Commercial aluminum bronzes usually contain 4 to 11% aluminum and may contain iron, nickel, manganese, and silicon. The corrosion rates of these in sea water vary almost linearly with water velocity which is the most important variable affecting general corrosion. Local accelerated attacks may occur in the form of pittings, crevice corrosion, impingement attack, dealuminization, and galvanic action. Dealuminization, which is recognized by a distinct copper color, appears most commonly at the waterline of partially immersed alloys. Crevice corrosion occurs in all specimens around and under their nonmetallic mountings and, occasionally, at sites where barnacles

are attached. Impingement attacks, which are associated with turbulent water flows, are commonly found at the inlet ends of condenser tubes and in pipe lines downstream from the fittings.

The potentials of aluminum bronzes and comparison alloys in sea water flowing at 13 ft. per sec were measured with a saturated calomel half-cell and a potentiometer. The potentials of aluminum bronzes (0.13 to 0.34) were comparable to those of other resistant materials used in sea water environments.

Heliarc and carbon arc welding produced no significant changes in the corrosion properties of alloys exposed in several environments. Also no serious galvanic corrosion occurred between the base alloys and weld deposits. Aluminum bronzes are not susceptible to stress-corrosion cracking in marine environments.

The bronzes are subject to varying degrees of fouling in quiet sea and brackish estuary waters. The amount of copper released by corrosion appears to be unrelated to the toxicity to fouling organisms. Fouling is not a problem at water velocities of 1.5 ft per sec or higher.

Corrosion fatigue properties of aluminum bronzes compare favorably with those of other copper-base alloys. Resistance patterns in sea and brackish river water are similar.

Aluminum bronzes are used for salt water piping, condenser components, valve stems, propellers, and numerous other components in military and merchant vessels.

314

Williams, W. L. EFFECT OF CARBON CONTENT ON MARINE CORROSION RESISTANCE OF CAST 19-9 CR-NI STEEL. Navy Marine Engineering Lab. Report No. 040039A, AD- 23 781: September 1953.

315

Williams, W. L. METALS FOR HYDROSPACE. Journal of Materials, American Society for Testing and Materials. 2: No. 4: 769-800, December 1967.

Effective use of the under-sea frontier presents major challenges to metallurgists and materials engineers. These challenges are related to a need for high-performance alloys in pressure hulls, machinery, and auxiliary equipment operating under severe environmental conditions. Special problems and approaches to their solution are discussed in areas of design against brittle fracture, high- and low-cycle

fatigue, and various types of marine corrosion and their relation to ocean depth. Examples are given of steels, titanium alloys, and copper alloys developed primarily for deep-ocean technology. Attention is given throughout to the relation between material-property data and performance of actual equipment. Finally, brief mention is made of metallurgical problems in construction of large tanks in which structures and machinery can be tested under simulated deep-ocean conditions.

296

Zanis, C. A., Crisci, J. R. EFFECTS OF WELDING AND POST-WELD HEAT TREATMENT ON THE SEA WATER CORROSION RESISTANCE OF MANGANESE-NICKEL-ALUMINUM BRONZE. Naval Applied Science Lab., Report No. NASL-930-76-PR-4, AD-861 871L: 28 p., November 1969.

297

Zeiger, H. CORROSION RESISTANCE OF ALUMINUM IN CONTACT WITH OTHER METALS. Aluminium, Paris, 37: No. 5: 284-288, May 1961.

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## PROPELLANTS AND EXPLOSIVES

C. L. Whitman  
Naval Ordnance Station  
Indian Head, Maryland

### INTRODUCTION

Ocean technology tasks, particularly salvage or rescue operations, may involve direct handling of submerged ordnance and similar items which present a considerable safety hazard. All submerged items must be presumed to be in the original and hazardous state unless proven otherwise. It is therefore important to know what kind of behavior to expect from potentially dangerous submerged ordnance components, such as propellants and explosives.

Consideration of the effect of seawater on ordnance is complicated by the wide and seasonal variations in pressure, temperature, salinity, biological agents, oxygen, and solar radiation that may be encountered. Resistance of ordnance items to pressure and to corrosion varies; although the cases are usually sealed, they will leak at rates differing with conditions. In addition the item submerged will affect the immediate environment, with the greatest effect occurring in interior areas. Leaching of salts, oxidizers, and antibiologics; corrosion of metals; electrolytic couples; precipitation; and other interreactions will modify and change the rate of degradation. The net effect of submersion on ordnance, therefore, is difficult to predict except in a general statement unless the specific prevailing conditions are accurately known.

Tests of the action of seawater on propellants and explosives have not been extensive. In addition pertinent information is well buried in files, and retrieval is difficult or impossible.

### GENERAL NATURE AND INGREDIENTS OF PROPELLANTS

Even though direct correlation between the effects on single ingredients and materials *in situ* may not always be possible, still it is convenient to start this study with consideration of the effect of seawater immersion on these isolated elements. Such a simplified approach immediately suggests the importance of solubility, state (liquid or solid), biological action, and hydrolysis in the degradation and deactivation processes.

Table 5 gives a comprehensive list of ingredients under common names and commonly used designations or abbreviations. Various grades of some materials may be used, such as nitrocellulose with different nitrations and degrees of polymerization or aluminum with a range of particle sizes. In these cases Table 5 considers the average grade only. Materials are further altered in curing of composite propellants, as when polyols are reacted to form urethanes or when liquid polybutadiene is crosslinked to form elastomers. In these cases the table considers the resulting material rather than the parent compound. The last three columns of the table assume that the ingredient is wet with a large but finite volume of seawater at elevated pressure with the temperature at or near 25°C.

Propellants are compounded from the ingredients shown in Table 5 and may contain from two to 20 ingredients. These propellants are fuel/oxidizer systems with ingredients added as stabilizers, plasticizers, catalysts, and modifiers and for other purposes as indicated in the table. Usually, however, any single ingredient acts in a multifunctional role, with nitroglycerine being an oxidizer, fuel, and plasticizer, diphenylamine being a stabilizer and fuel, dibutyl phthalate being a fuel and plasticizer, etc. Therefore the loss of one or more of the ingredients by solution or degradation or the addition of salt water may seriously impair the functioning of the unit. As a general rule, solid propellants, except those containing large amounts of water-soluble material, will fire when wet, but performance when wet or after drying will be

Table 5  
Effect of Seawater on Propellant and Explosive Ingredients

Compound	Designation	Principal Use	Normal State	Soluble in Water	Effect of Seawater*	Estimated Life in Seawater*	Ignitable Under Water
Diphenylamine	DPA	Stabilizer	Solid	Slightly	Ox	5 years	No
Dipropyl adipate	DNPA	Fuel, plasticizer	Liquid	Slightly	Ox, Bi, Hy	5 years	No
Ethyl cellulose	—	Fuel, binder, inhibitor	Solid	Insoluble	Sw, Bi, Ox	5 years	No
Ethylene glycol dinitrate	EGDN	Oxidizer	Liquid	Slightly	Rd, Bi, Hy	5 years	Yes
Ferric acetylacetonate	FeAA	Catalyst	Solid	Slightly	Ox, Bi	1 year	No
Ferric octoate	—	Catalyst	Solid	Slightly	Ox, Bi	1 year	No
Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>	Catalyst	Solid	Insoluble	—	—	No
Ferrocene	—	Catalyst	Solid	Insoluble	Bi, Ox	2 years	No
Graphite	—	Antistatic	Solid	Insoluble	—	—	No
Guanidine nitrate	—	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 year	No
Guanidine perchlorate	—	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 year	No
Hydroxylammonium nitrate	HAN	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 month	No
Hydroxylammonium perchlorate	HAP	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 month	No
Hydrazine nitrate	HN	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 month	No
Hydrazine perchlorate	—	Oxidizer	Solid	Soluble	Rd, Bi, Hy	1 month	No
Isoprene	—	Fuel, binder	Solid	Insoluble	Bi, Ox	5 years	No
Lead azide	—	Explosive	Solid	Insoluble	Ox	5 years	Yes
Lead carbonate, basic	—	Catalyst	Solid	Insoluble	—	—	No
Lead 2-ethylhexoate	—	Catalyst	Viscous	Insoluble	Hy, Ox	1 year	No
Lead maleate	Tri-Mal	Catalyst	Solid	Insoluble	Ox, Hy	5 years	No
Lead dioxide	PbO <sub>2</sub>	Oxidizer	Solid	Insoluble	Rd	5 years	No
Lead β resorcyate	—	Catalyst	Solid	Insoluble	Ox, Hy	1 year	No
Lead salicylate	—	Catalyst	Solid	Insoluble	Ox, Hy	1 year	No
Lead stearate	—	Catalyst	Solid	Insoluble	Ox, Hy	5 years	No
Lead styphnate	—	Explosive	Solid	Insoluble	Rd	5 years	Yes
Lead styphnate, basic	—	Explosive	Solid	Insoluble	Rd	5 years	Yes
Lead thiocyanate	Pb(SCN) <sub>2</sub>	Explosive	Solid	Insoluble	—	—	Yes
Lithium hydride	LiH	Fuel	Solid	Reacts	Rea	1 day	No
Lithium perchlorate	LiClO <sub>4</sub>	Oxidizer	Solid	Soluble	Rd	1 month	No
Magnesium	Mg	Fuel	Solid	Reacts	Rea, Ox	2 years	No
Magnesium carbonate	MgCO <sub>3</sub>	Buffer	Solid	Insoluble	—	—	No
Magnesium oxide	MgO	Catalyst	Solid	Insoluble	—	—	No
Mercury fulminate	—	Explosive	Solid	Insoluble	Ox	5 years	Yes
Milori blue	—	Catalyst	Solid	Insoluble	Ox	5 years	No
Nitric acid	RFNA, HNO <sub>3</sub>	Oxidizer	Liquid	Soluble	Rd, Bi	1 week	No
Nitrocellulose	NC	Oxidizer, fuel, binder	Solid	Insoluble	Rd, De, Bi, Hy, Sw	4 years	Yes
2-Nitrodiphenylamine	2NDPA	Stabilizer	Solid	Slightly	Ox	5 years	No
Nitroglycerin	NG	Oxidizer	Liquid	Slightly	Rd, Bi, Hy	3 years	Yes
Nitroguanidine	NQ	Oxidizer	Solid	Soluble	Bi, Hy, Rd	1 year	No
Nitrostarch	NS	Oxidizer, binder	Solid	Insoluble	Bi, Rd, Hy, Sw	3 years	Yes
Nylon	—	Binder	Solid	Insoluble	Bi, Ox	5 years	No
Oxamide	—	Fuel	Solid	Insoluble	Bi, Ox	2 years	No
Pentaerythritol tetranitrate	PETN	Explosive	Solid	Slightly	Bi, Rd, Hy	4 years	Yes
Phenyl β naphthylamine	PBNA	Stabilizer	Solid	Insoluble	Ox	2 years	No
Polybutadiene, crosslinked	—	Binder	Solid	Insoluble	Bi, Ox, Hy	5 years	No
Polybutadiene, liquid	—	Plasticizer	Liquid	Insoluble	Bi, Ox, Hy	2 years	No
Polybutadiene, crosslinked copolymers	—	Binder	Solid	Insoluble	Bi, Ox, Hy	5 years	No
Polyester, crosslinked	—	Binder	Solid	Insoluble	Bi, Ox, Hy	5 years	No
Polyester, crosslinked copolymer	—	Binder	Solid	Insoluble	Bi, Ox, Hy	8 years	No
Polyfluoro vinylidene	Viton A	Binder, thermite	Solid	Insoluble	—	—	No
Polymethyl vinyl tetrazole	PMVT	Binder	Solid	Soluble (linear)	Bi, Ox, Sw	1 year	No
Polysulfide, crosslinked	—	Binder	Solid	Insoluble	Bi, Ox	5 years	No

(Table continues)

Table 5 (Continued)

Compound	Designation	Principal Use	Normal State	Soluble in Water	Effect of Seawater*	Estimated Life in Seawater*	Ignitable Under Water
Acetyl triethyl citrate	ATC	Plasticizer	Liquid	Slightly	Bi, Hy, Ox	1 year	No
Aluminum	Al	Fuel	Solid	Insoluble	Bi, Ox	1 year	No
Aluminum hydride	AlH <sub>3</sub>	Fuel	Solid	Reacts	Rea, Ox	1 week	No
Ammonium dichromate	(NH <sub>4</sub> ) <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	Oxidizer, catalyst	Solid	Soluble	Rd, Bi	1 week	No
Ammonium nitrate	AN	Oxidizer	Solid	Soluble	Bi, Rd	1 week	No
Ammonium oxalate	—	Fuel	Solid	Soluble	Bi, Ox	1 week	No
Ammonium perchlorate	AP	Oxidizer	Solid	Soluble	Rd, Bi	1 week	No
Ammonium picrate	D	Explosive	Solid	Soluble	Rd, Bi	1 year	No
Ammonium sulfate	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Fuel, oxidizer	Solid	Soluble	Bi, Rd	1 week	No
Aniline	C <sub>6</sub> H <sub>7</sub> N	Fuel	Liquid	Slightly	Ox	1 year	No
Barium nitrate	Ba(NO <sub>3</sub> ) <sub>2</sub>	Oxidizer, catalyst	Solid	Soluble	Rd	1 week	No
Barium peroxide	BaO <sub>2</sub>	Oxidizer	Solid	Slightly	Rd	1 year	No
Beryllium	Be	Fuel	Solid	Insoluble	Ox	2 years	No
Beryllium hydride	BeH <sub>2</sub>	Fuel	Solid	Reacts	Rea, Ox	1 day	No
Boron	B	Fuel	Solid	Insoluble	Ox	2 years	No
Butyl stearate	—	Plasticizer	Liquid	Slightly	Ox, Bi	1 year	No
Carbon black	CB	Fuel, catalyst	Solid	Insoluble	Ox	5 years	No
Cellulose acetate	CA	Fuel, binder	Solid	Insoluble	Hy, De, Sw, Bi	5 years	No
Charcoal	—	Fuel	Solid	Insoluble	Ox	5 years	No
Chlorine pentafluoride	ClF <sub>5</sub>	Oxidizer	Liquid	Reacts	Rea	1 week	No
Chlorine trifluoride	ClF <sub>3</sub>	Oxidizer	Liquid	Reacts	Rea	1 week	No
Copper chromite	—	Catalyst	Solid	Insoluble	—	10 years	No
Cupric salicylate, basic	MBCS	Catalyst	Solid	Insoluble	Hy	5 years	No
Cyclotetramethylene tetranitramine	HMX	Oxidizer, explosive	Solid	Insoluble	Hy, Bi, Rd	5 years	Yes
Cyclotrimethylene trinitramine	RDX	Oxidizer, explosive	Solid	Insoluble	Hy, Bi, Rd	5 years	Yes
Isodecyl pelargonate	IDP	Plasticizer, fuel	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Dibutyl phthalate	DBP	Plasticizer, fuel	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Dibutyl sebacate	DBS	Plasticizer, fuel	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Diethyl diphenylurea	Centralite I	Stabilizer	Solid	Insoluble	Ox	5 years	No
Diethylene glycol dinitrate	DEGDN	Oxidizer, explosive	Liquid	Slightly	Rd, Bi, Hy	5 years	Yes
Diethyl phthalate	DEP	Plasticizer, fuel	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Dimethyl diphenylurea	Centralite II	Plasticizer, fuel	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Dimethyl hydrazine	UDMH	Liquid, fuel	Liquid	Soluble	Ox, Bi	1 year	No
Bis-dinitrophenoxy ethane	—	Fuel, oxidizer	Solid	Insoluble	Rd, Bi	5 years	Yes
Dinitrophenoxy ethanol	—	Fuel, oxidizer, plasticizer	Solid	Slightly	Rd, Bi	2 years	Yes
Bis-dinitropropyl acetal	BDNPA	Fuel, oxidizer, plasticizer	Liquid	Slightly	Rd, Bi	5 years	Yes
Bis-dinitropropyl formal	BDNPF	Fuel, oxidizer, plasticizer	Liquid	Slightly	Rd, Bi	5 years	Yes
Dinitrotoluene	DNT	Fuel, oxidizer, plasticizer	Solid	Slightly	Rd	5 years	Yes
Diocetyl adipate	DOA	Fuel, plasticizer	Liquid	Insoluble	Ox, Bi, Hy	5 years	No
Diocetyl phthalate	DOP	Fuel, plasticizer	Liquid	Insoluble	Ox, Bi, Hy	5 years	No

(Table continues)

Table 5 (Continued)

Compound	Designation	Principal Use	Normal State	Soluble in Water	Effect of Seawater*	Estimated Life in Seawater*	Ignitable Under Water
Polytetrafluoroethylene	Teflon	Binder, thermite	Solid	Insoluble	—	—	No
Polyurethane, crosslinked	—	Binder	Solid	Insoluble	Bi, Ox, Hy	5 years	No
Polyvinyl chloride	PVC	Binder	Solid	Insoluble	Bi, Ox, Hy	10 years	No
Potassium nitrate	KNO <sub>3</sub>	Oxidizer	Solid	Soluble	Bi, Rd	1 year	No
Potassium perchlorate	KClO <sub>4</sub>	Oxidizer	Solid	Slightly	Bi, Rd	5 years	Yes
Potassium sulfate	K <sub>2</sub> SO <sub>4</sub>	Flash suppressor	Solid	Soluble	Bi, Rd	1 year	No
Propylene glycol dinitrate	PGDN	Oxidizer	Liquid	Slightly	Bi, Hy, Rd	3 years	Yes
Red lead	Pb <sub>3</sub> O <sub>4</sub>	Oxidizer	Solid	Insoluble	—	—	No
Resorcinol	—	Stabilizer	Solid	Soluble	Ox	2 years	No
Silicon	Si	Fuel	Solid	Insoluble	Ox	3 years	No
Silicon	—	Catalyst	Solid	Insoluble	—	—	No
Silver iodate	AgIO <sub>3</sub>	Oxidizer	Solid	Slightly	Bi, Hy, Rd	1 year	Yes
Sodium barbiturate	—	Catalyst	Solid	Soluble	Bi, Ox, Hy	1 year	No
Sodium nitrate	NaNO <sub>3</sub>	Oxidizer	Solid	Soluble	Rd, Bi	1 year	No
Sorbitol pentanitrate	SPN	Oxidizer	Viscous	Insoluble	Bi, Hy, Rd	4 years	Yes
Sulfur	S	Fuel, catalyst	Solid	Insoluble	Bi, Ox	5 years	No
Sucrose octacetate	SOA	Plasticizer	Solid	Slightly	Ox, Bi, Hy	3 years	No
Tetracene	—	Explosive	Solid	Slightly	Bi, Hy	5 years	Yes
Tetryl	—	Explosive	Solid	Insoluble	Hy, Rd	3 years	Yes
Tin	Sn	Fuel	Solid	Insoluble	Ox	—	No
Triaminoguanidine nitrate	TAGN	Oxidizer	Solid	Soluble	Hy, Rd, Bi	1 year	No
Triethyl citrate	—	Plasticizer	Liquid	Slightly	Bi, Ox, Hy	2 years	No
Triethylene glycol dinitrate	TEGDN	Oxidizer	Liquid	Slightly	Bi, Hy, Rd	3 years	Yes
Trimethylolethane trinitrate	MTN, TMETN	Oxidizer	Liquid	Insoluble	Hy, Bi, Rd	5 years	Yes
Trinitrotoluene	TNT	Explosive	Solid	Slightly	Rd	5 years	Yes
Tungsten	W	Fuel	Solid	Insoluble	Ox	5 years	No
Zirconium	Zr	Fuel	Solid	Insoluble	Ox	—	No

\*Bi = biodegrades; De = decomposes; Hy = hydrolyzes; Ox = oxidizes; Rea = reacts; Rd = reduces; Sw = swells.

unsatisfactory. Some solid propellants may be successfully reworked and most may be identified with some precision even after long immersion. A classification of propellants (and explosives) into classes and types is given in Table 6.

Table 6  
Classification of Propellants

Class	Type
Nitrocellulose base	Single base, double base, triple base, composite modified double base*
Composite	Linear binders,* crosslinked binders,* fuel-rich composites
Liquid	Monopropellants, binary systems
Hybrid	Liquid-solid systems

\*May also be used as explosives.

## Nitrocellulose Propellants

Four propellant compositions are nitrocellulose based. In addition to their own specific properties, all the formulations contain stabilizers to inhibit autocatalytic decomposition by removing free  $\text{NO}_2$  from the system. These stabilizers also act as free-radical scavengers, antioxidants, and antibiological agents.

**Single Base** — Single-base propellants, which are used exclusively as gun propellants, are hard strong colloids that age relatively slowly in seawater. These propellants have been recovered from sunken ships, reworked, and used. In addition propellants for the 20-, 30-, and 50-mm weapons have a deterrent coating of DNT, ethyl centralite, dibutyl phthalate, or combinations thereof. These coatings, especially DNT and EC, would tend to inhibit biological degradation but would complicate reclamation. The information on single-base gun propellants is included in Table 7.

**Double Base** — Double-base propellants are softer, have shorter shelf lives, and are more subject to leaching by seawater than are single-base compositions. Flake or ball double-base propellants with high surface-to-volume ratios are used in ammunition for pistols, shotguns, and rifles. These are more liable to degrading attack than are the denser lower-surface-to-volume grains used in larger caliber weapons. A double-base composition is also used in mortar propellants and in many rocket motors. The mortar propellants are sheets or small extruded grains which are designed with relatively high surface-to-volume ratios and high burning rates; the composition and properties of these (Table 8) are similar to those of the double-base formulations shown in Table 7.

Small rocket grains are formed by extrusion, and large ones are formed by casting. Grain diameters for gas generators and cartridge actuating devices may range from a few inches up to 4 feet for large booster/sustainer units. Lengths vary from inches to 12 feet. These grains are mechanically strong colloids or plastics that are permeated only slowly by water. In equilibrium with liquid water at ambient temperatures and pressures the propellant contains 2 to 3% water, depending on the specific composition. The initial and immediate effect of water is a decrease of the mechanical strength, and this effect is reversible. The long-term effect is hydrolysis of the polymer and plasticizers, nitration and oxidation of the stabilizer, and hydrolysis and oxidation of the ballistic modifiers in nonreversible reactions. In the presence of biologically active agents the hydrocarbons and nitrates are consumed. The rate of leaching of soluble salts is low. If aluminum has been added in small concentrations for suppression of resonant burning and to increase delivered energy levels, the aluminum would not be rapidly attacked by salt water due to the passivation of the metal by nitrates and low transport of salt through the colloid.

**Triple Base** — Triple-base propellants (Table 7) have been used exclusively for guns larger than 3 inches but have been essentially phased out. They contain up to 60% nitroguanidine, which is subject to serious leaching by water, and the basic products resulting from decomposition of the nitroguanidine greatly increases the degradation of the remaining propellant. Rework of these propellants after short immersions would not be practical.

**Composite Modified Double Base** — The properties of composite modified double-base propellants and their reactions to seawater (Table 9) are quite different from those of orthodox materials. The composite modified double-base propellants contain nitrocellulose, nitroglycerin, ammonium perchlorate, HMX, aluminum, stabilizers, and plasticizers in various combinations. Water dissolves the relatively high percentages of soluble salts in the structure. The concentrated solutions of ammonia together with the salt present in seawater corrode the aluminum with generation of hydrogen. The resorcinol used as one stabilizer and other water-soluble materials are lost by leaching. The remaining porous network softens and then collapses; subsequent hydrolysis and disintegration of everything except the HMX follows.

Table 7  
Effect of Seawater on Gun Propellants

Type	Principal Ingredients	Type of Coating	Form	Life in Seawater (years)	Identifiable After Immersion	Ignitable When Wet	Usable When Wet	Usable After Drying	Reworkable
Small Arms									
Double base	NC, NG, stabilizer, plasticizer, water	Graphite	Flake or ball	5	Yes	Yes	No	No	Yes
Small-Caliber Guns									
Single base	NC, stabilizer, solvent, water	DNT, EC, or DBP plus graphite	Cylinder, single perforation	10	Yes	Yes	No	No	Yes
Single base	NC, DNT, DBP, stabilizer, solvent, water	DNT, EC, or DBP plus graphite	Cylinder, single perforation	10	Yes	Yes	No	No	Yes
Large-Caliber Guns									
Single base	NC, stabilizer, solvent, water	None	Cylinder, seven perforations	10	Yes	Yes	No	No	Yes
Single base	NC, DNT, DBP, stabilizer, solvent, water	None	Cylinder, seven perforations	10	Yes	Yes	No	No	Yes
Triple base	NC, NG, NQ, stabilizer, plasticizer, solvent, water	None	Cylinder, seven perforations	2	Yes	Doubtful	No	No	Doubtful

Table 8  
Effect of Seawater on Double-Base Rocket Propellants

Application	Composition	Shelf Life (years)	Life in Seawater (years)	Ignitable In Water	Usable When Wet	Usable After Drying*	Reworkable
Motors and cartridge actuating devices in sheets or small grains	NC, NG, stabilizer, plasticizer, $\text{KNO}_3$ or $\text{Ba}(\text{NO}_3)_2$	10	5	Yes	No	Yes	Yes
Rockets and gas generators in small to large grains	NC, NG, stabilizer, plasticizer, modifiers	5 to 8	5	Yes	No	No <sup>†</sup>	No <sup>†</sup>
Rockets and gas generators in small to large grains	NC, NG, stabilizer, plasticizer, modifiers, Al	5 to 8	3 to 5	Yes	No	No <sup>†</sup>	No <sup>†</sup>

\*Assuming a short immersion time.

<sup>†</sup>Possible but not practical.

Table 9  
Effect of Seawater on Composite Modified Double-Base Propellant

Composition	Shelf Life (years)	Life in Seawater (years)	Ignitable in Water	Usable When Wet	Usable After Drying*	Reworkable
NC, NG, stabilizers, $\text{NH}_4\text{ClO}_4$ , Al, plasticizers	5	1	Yes	No	No	Doubtful <sup>†</sup>
NC, NG, stabilizers, $\text{NH}_4\text{ClO}_4$ , Al, plasticizers, HMX	5	1	Yes	No	No	Doubtful <sup>†</sup>

\*Assuming a short immersion time.

<sup>†</sup>The procedures are complicated and possibly impractical.

### Composite Propellants

Modern composite propellants (Table 10) comprise a large and varied family. Grains range from small units used in gas generators to large masses used in ICBM boosters. Small grains may be formed by pressure molding, extrusion, or casting, and large assemblies are cast. Grains may be cartridge loaded or case bonded (cast in place). In general, composites may be described as solid oxidizers and fuels loaded in polymeric binders with the solids comprising as high as 88% of the propellant weight. Binders may be linear polymers such as polyvinyl chloride and cellulose acetate or may be crosslinked rubbers such as urethanes and polybutadienes cured in situ. Many other ingredients may be added for alteration of ballistic properties, mechanical properties, or flame temperature or to achieve other specific effects. All formulations contain stabilizers and antioxidants or other substances that will inhibit biological attack. Like double-base propellants, composites will absorb water until equilibrium is

Table 10  
Effect of Seawater on Composite Propellants

Composition	Type of Binder	Initial Effect of Water	Long Term Effect of Water	Life in Seawater (years)	Identifiable After Immersion	Ignitable When Wet	Usable When Wet	Usable After Drying	Reworkable
With Ammonium Nitrate									
Isoprene, $\text{NH}_4\text{NO}_3$ , catalysts, curatives	Crosslinked	Strong swelling, leaching	—	1	—	No	No	No	No
Cellulose acetate, $\text{NH}_4\text{NO}_3$ , plasticizers, catalysts	Linear	Strong swelling, leaching	—	1	—	No	No	No	No
Polybutadiene-methylvinylpyridine, $\text{NH}_4\text{NO}_3$ , plasticizers, catalysts	Crosslinked	Strong swelling, leaching	—	1	—	No	No	No	No
Stable Compositions									
Polyvinyl chloride, $\text{NH}_4\text{ClO}_4$ , plasticizer, stabilizer	—	Slight swelling, some leaching	Leaching, split-off HCl, complete degradation	10	—	Yes	No	No	No
Polyester, $\text{KClO}_4$	—	Very slight swelling	Slow leaching, chain scission, complete degradation	10	—	Yes	No	No	No
Teflon, Viton A, $\text{NH}_4\text{ClO}_4$ , Al	—	Almost none	Leaching, corrosion of Al	10	—	Yes	No	No	No
General Compositions									
Urethane, $\text{NH}_4\text{ClO}_4$ , plasticizer, stabilizer	—	Swelling, leaching	—	3 to 5	Yes	Yes	No	No	No
Urethane, $\text{NH}_4\text{ClO}_4$ , Al, plasticizers, stabilizers	—	Swelling, leaching, corroding	—	3	Yes	Yes	No	No	No
Polybutadiene, $\text{NH}_4\text{ClO}_4$ , Al, plasticizers, stabilizers	—	Swelling, leaching, corroding	—	3	Yes	Yes	No	No	No
Polysulfide, $\text{NH}_4\text{ClO}_4$ , plasticizers	—	Swelling, leaching	—	3 to 5	Yes	Yes	No	No	No
Polyurethane, $\text{NH}_4\text{ClO}_4$ , BDNPA or BDNPF, Al	—	Strong swelling	—	2 to 4	Yes	Yes	No	No	No
Polybutadiene, $\text{KClO}_4$ , $\text{Pb}(\text{NO}_3)_2$ , Al	—	Swelling	—	5 to 8	Yes	Yes	No	No	No
Polyester, HMX	—	Slight swelling	—	5 to 8	Yes	Yes	No	No	No

established. The initial and reversible effect of absorbed water lowers mechanical properties; the leaching and later hydrolytic, corrosive, degradative, and oxidative reactions are irreversible.

Fuel-rich composite propellants are used in air-augmented motors. The two current service versions contain polybutadiene/Al/ $\text{NH}_4\text{ClO}_4$  or polybutadiene/B/ $\text{NH}_4\text{ClO}_4$ . These burn rapidly and completely in air but incompletely without a supply of extra oxygen. These are less hazardous under water than are balanced composites. Otherwise their properties will be similar to those given in Table 10 for the polybutadiene-based propellants containing aluminum.

## Liquid Propellants

Some rocket motors are powered by liquid propellants. A common arrangement for these systems is separate tankage for oxidizers and fuels. An example of this is found in the red-fuming-nitric-acid/unsymmetric-dimethyl-hydrazine system. When the two components are mixed, they are hypergolic (self-igniting). The fuels will also burn in air; they may present a corrosion or toxicity problem. The oxidizers are mostly soluble in or react with water. Under certain conditions they may decompose rapidly in air with explosive force, and they are corrosive and toxic. Considered separately these fuels and oxidizers have the properties indicated in Table 5.

Liquid monopropellants are storable mixtures of fuel and oxidizer with other ingredients added to impart specific properties. The only one in service use is Otto Fuel II, a mixture of propylene glycol dinitrate, dibutyl sebacate, and 2-nitrodiphenylamine, used in the Mark 46 and 48 torpedoes. This material is slightly volatile, slightly soluble in water, and in general will show reactions in seawater similar to those of double-base propellants. The probable life in seawater should be 2 to 4 years. The practicality of rework after significant exposure to seawater is doubtful. Advanced liquid monopropellants are being studied or are in development. The most promising of those, hydroxylammonium perchlorate/organic solvent/water and perchloric acid/piperidine/water are quite water soluble and will disperse rapidly in the sea without leaving dangerous residues.

## Hybrid Propellants

Hybrid propellants are those using liquid oxidizers and solid fuel grains. Simple fuels such as polyethylene are inert but will burn in air; in relatively massive form they may survive in water for long periods without appreciable change. Those containing free metal such as aluminum, magnesium, or boron are only slightly more hazardous in air and will not burn in water; in seawater the metals corrode, and their probable lives are not greater than 5 years. Fuel grains containing metal hydrides such as  $\text{LiH}$ ,  $\text{AlH}_3$ , or  $\text{BeH}_2$  will burn rapidly in air and will react rapidly with water to form hydrogen. Their life expectancy in water, even when they are massive, is quite short, possibly less than 1 week. Liquid oxidizers such as those used in binary liquid systems are used in these hybrid systems. Properties of the oxidizers are as given in Table 5.

## EXPLOSIVES AND IGNITION-ELEMENT, TIME-DELAY, AND TRACER COMPOSITIONS

Compositions used in squibs, igniters, and fuses are usually, but not always, easily ignited mixtures (Table 11). They are designed to produce hot gases, hot particles, or both. These formulations must ignite on demand and burn to produce the required heat or pressure in a specified short time. Traces of water therefore can adversely affect proper functioning, and large quantities of water can completely inhibit action. Many of these compositions, such as black powder, contain essential but highly soluble ingredients. These compositions are used in small quantities, and usually the surface-to-volume ratio is high. Seawater therefore will have a more immediate and drastic effect on these compositions than on the massive and well-consolidated propellants. They may be deactivated in a few minutes in excess water and completely leached in a few hours. In these cases direct identification is impossible, but a reasonably probable conclusion can be obtained by careful examination of residues. Thus a residue of graphite, charcoal, and sulfur can identify black powder by inference.

Time-delay compositions (Table 12) are frequently used in conjunction with propellants and explosives. These powders with high surface-to-volume ratios are used to delay action from the initial trigger to the final ignition. The burning rate must be finely controlled, and minor amounts of water affect performance drastically. The initial effect of water slows the burning rate, since heat is removed by vaporization of the liquid. As a permanent effect, water alters the surface properties of the fuel (metal) and slows the advance of the flame front.

Table 11  
Effect of Seawater on Ignition — Element Compositions

Type and Composition	Life in Water	Identifiable After Immersion	Ignitable When Wet	Ignitable After Drying	Usable When Wet	Usable After Drying	Reworkable
Squib, Igniter, and Fuse Compositions							
Percussion igniter — mercury fulminate, $KClO_3$ , $Sb_2S_3$	1 year	Yes*	Yes	Yes	—	—	No
Black powder — $KNO_3$ , charcoal, S, graphite	1 hour	Yes*	No	No	—	—	No
B, $KNO_3$	1 hour	Yes*	No	No	—	—	No
Hot spot — Mg, Teflon	10 years	Yes	Yes	Yes	—	—	No
Hot spot/pressure — Al, $NH_4ClO_4$ , oil	1 day	Yes*	No	No	—	—	No
ALA — Zr, $Fe_2O_3$ , $SiO_2$	5 years	Yes	Yes	Yes	—	—	No
Percussion Primer Compositions							
$KClO_3$ , $Ba(NO_3)_2$ , $Pb(CNS)_2$ , glass, TNT	1 week	Yes*	Yes	—	No	No	No†
Basic lead styphnate, tetracene, $Ba(NO_3)_2$ , $Sb_2S_3$ , Al	1 to 2 years	Yes*	Yes	—	No	No	No†
$KClO_3$ , $Sb_2S_3$ , $Pb(CNS)_2$ , TNT	1 to 2 months	Yes*	Yes	—	No	No	No†
Lead styphnate, tetracene, $Ba(NO_3)_2$ , $Sb_2S_3$ , Zr, $PbO_2$ , TNT	1 to 2 years	Yes*	Yes	—	No	No	No†
Electric Primer Compositions							
$KClO_3$ , lead nitroresorcinate, NC	1 year	Yes*	Yes†	—	No	No	No†
$KClO_3$ , $Pb(CNS)_2$	1 year	Yes*	Yes†	—	No	No	No†
$KClO_3$ , diazo dinitrophenol (DDNP)	1 year	Yes*	Yes†	—	No	No	No†
$KClO_3$ , DDNP, charcoal, nitrostarch	1 year	Yes*	Yes†	—	No	No	No†

\*By inference from related residue.

†Not feasible.

‡With heat.

Table 12  
Effect of Seawater on Time-Delay Compositions

Composition	Life in Water (years)	Identifiable After Immersion	Ignitable When Wet	Usable When Wet	Usable After Drying	Reworkable
Si, Pb <sub>3</sub> O <sub>4</sub> , NC, camphor	1	Yes	Yes	No	No	No*
B, BaCrO <sub>4</sub>	1	Yes	Yes	No	No	No*
Zr/Ni alloy, BaCrO <sub>4</sub> , KClO <sub>4</sub>	1	Yes	Yes	No	No	No*
Mg, BaCrO <sub>4</sub> , PbCrO <sub>4</sub>	1	Yes	Yes	No	No	No*
W, BaCrO <sub>4</sub> , KClO <sub>4</sub> , SiO <sub>2</sub>	1	Yes	Yes	No	No	No*
Cr, BaCrO <sub>4</sub> , ClO <sub>4</sub>	1	Yes	Yes	No	No	No*

\*Possible but not practical.

Tracer compositions (Table 13), which are placed in small amounts in a cavity at the fore end of a projectile, are similar in many respects to ignition and time-delay materials. Since tracer compositions are exposed to weather and spray at times, they must be reasonably waterproof and durable. Tracers are used with ammunition for small-caliber guns to provide a line of sight for directing fire; performance, especially in bright sunlight, is not critical for proper functioning of the round.

Table 13  
Effect of Seawater on Tracer Compositions

Composition	Life in Water (years)	Identifiable After Immersion	Ignitable When Wet	Reworkable
Mg, BaO <sub>2</sub> , asphalt	1	Yes*	Yes	No†
Mg, SrO <sub>2</sub> , zinc stearate	1	Yes*	Yes	No†
Mg, Sr(NO <sub>3</sub> ) <sub>2</sub> , KClO <sub>4</sub> , strontium oxalate, calcium resinate	1	Yes*	Yes	No†
Mg, Ba(NO <sub>3</sub> ) <sub>2</sub> , barium oxalate, binder	1	Yes*	Yes	No†
Mg, Sr(NO <sub>3</sub> ) <sub>2</sub> , sodium oxalate, binder	1	Yes*	Yes	No†
Mg, Ba(NO <sub>3</sub> ) <sub>2</sub> , binder	1	Yes*	Yes	No†

\*By inference.

†Possible but not practical.

Warheads with their attendant explosive charges, time-delay fuses, detonators, electronic components, and hardware constitute the payload delivered by most gun and rocket systems. Detonators are either lead azide formulations, mercury fulminate mixtures as shown in Table 11, or similar in composition and properties to the percussion igniters of Table 11.

Booster explosives, usually PETN, tetryl, or RDX/wax may be used in relatively small amounts to amplify the action of the detonator; properties of these will be as shown in Table 5. Main bursting charges may be small or very large projectiles, underwater mines, and large aerial bombs. Usually the cavities are well sealed within the hardware, and the probability that the charges will get wet when immersed in seawater is small. Units under water may be

expected to last a long time. In some cases mines designed for underwater use have functioned after 25 years of submersion. If the hardware is breeched and the explosive is wetted by the seawater, some charges such as TNT in massive form will persist for long times, whereas others such as ammonium picrate are appreciably soluble in water and will be dissipated shortly. The effects of seawater on some high explosives are shown in Table 14.

#### ASSEMBLED ORDNANCE

Ordnance ready for use acts or reacts quite differently in seawater than do ingredients or compounded mixtures. These devices and their packaging are designed to withstand rough field and combat usage. The contents are afforded reasonable protection against liquid and vaporized water, and many articles will survive submersion at moderate depths. The number of failures will increase with increasing depth, with only those items in extremely heavy cases such as bombs, projectiles, and warheads able to resist the crushing pressures at greater depths. In general, large articles and rocket motors (with tender weather seals) will be wetted more often at any given depth than small objects such as ammunition for small guns. Cases may also be breeched by mechanical damage such as that resulting from collapsing bulkheads and impact from hitting bottom. Corrosion during long-term submersion may result in failure of metal cases, and some plastic fittings may be less durable than metal when subjected to the byproducts of propellant/water reactions. The net result is that one cannot predict whether any article of ordnance has been breeched and wetted if submerged at moderate depth. All submerged items must be presumed to be in the original and hazardous state unless proven otherwise.

#### Ammunition for Small Arms

Ammunition for small arms is furnished in assembled charges. A shotgun round consists of a plastic case, a brass end-cap with a percussion igniter, plastic wads, chilled shot or lead slug, and rapid-burning double-base propellant. Rounds for pistols and rifles have brass cases with percussion igniters, brass projectiles over steel cores, paper or plastic wads, and double-base propellant. Cartridges are packed in cardboard boxes, and these boxes are further packed in waterproof ammunition cases of galvanized steel. These rounds are small and fairly waterproof. Many will remain hazardous even when submerged at moderately high pressures for long periods. Rounds not wetted can be salvaged and used in emergency situations. They can be recovered, identified, and characterized. Since each individual cartridge is small and rework entails large handling costs, salvage is probably not economically feasible.

#### Ammunition for Small-Caliber Guns

Ammunition for small-caliber weapons is similar in construction to rifle cartridges. The warheads of these larger rounds may have bursting charges and some may be tracer rounds. Methods of handling and stowage are similar to those used for small-arms ammunition. In general, cartridges recovered from shallow water after short-term immersion can be identified and characterized. Items from dry cases can be used in emergency situations. The feasibility of general use of dry rounds or of reworking large numbers of salvaged items is questionable.

#### Ammunition for Large Caliber Guns

Ammunition for large guns, up to and including some 5-inch, 54-caliber rounds, are assembled like the smaller cartridge cases. Projectiles are of steel, and all projectiles carry bursting charges. They may have proximity fuses, time delays, and other associated devices. Ignition is by an electrical squib, which ignites a secondary larger black-powder charge which, in turn, fires the propellant. These rounds may be quite large and therefore more subject to crushing by hydrostatic pressure or leakage at the seal between projectile and case. Some of these rounds may remain dry in shallow to moderately deep water for long times. They can be recovered, identified, and evaluated. Since failure of a charge can be catastrophic, it is

Table 14  
Effect of Seawater on Explosives

Name	Composition	Initial Effect of Seawater	Life in Seawater (years)	Detonable When Wet	Detonable After Drying	Usable When Wet	Usable After Drying	Reworkable
Amatol	NH <sub>4</sub> NO <sub>3</sub> , TNT	NH <sub>4</sub> NO <sub>3</sub> dissolves	1	No	No	No	--	Yes
Tritonal	TNT, Al	Al corrodes NO <sub>2</sub> groups reduce	1 to 2	Yes	Yes	Doubtful*	--	Yes
Pentolite	TNT, PETN	Little, if any	Over 5	Yes	Yes	Doubtful*	--	Yes
Tetrytol	Tetryl, TNT	Little, if any	Over 5	Yes	Yes	Doubtful*	--	Yes
Picrotol	TNT, D	D dissolves	1 to 3	Yes	Yes	No	--	Yes
PBXN-5	RDX, Viton A	--	Over 5	Yes	Yes	No	--	Yes
Ednatol	TNT, EDNA	--	2 to 4	Yes	Yes	Doubtful*	Yes	Yes
Composition B	RDX, TNT, wax	--	5 to 8	Yes	Yes	Doubtful*	Yes	Yes
Torpex	TNT, RDX, Al	--	2	Yes	Yes	Doubtful*	Doubtful	Doubtful
Composition A3	RDX, wax	--	5 to 8	Yes	Yes	Doubtful*	Yes	Yes
Composition C3	RDX, polyisobutylene, nitrotoluene, DNT, TNT, NC	--	5	Yes	Yes	Doubtful*	Yes	Yes
HBX	TNT, RDX, Al, wax	--	2 to 4	Yes	Yes	Doubtful*	Doubtful	Doubtful
PBXN-103	NC, NH <sub>4</sub> ClO <sub>4</sub> , 2NDPA, MTN, TEGDM	--	2 to 3	Yes	Yes	No	No	No
PBXW-106	RDX, urethane, BDNPA, BDNPF	--	2 to 3	Yes	Yes	Doubtful*	Yes	Doubtful
Octol	TNT, HMX	--	5 to 10	Yes	Yes	Doubtful*	Yes	Yes

\*Detonation may be incomplete.

probably inadvisable to attempt use of salvaged rounds except in cases of great emergency. These shells do represent a considerable investment in hardware, recoverable propellant, and explosive. Rework of such salvaged ammunition, especially that for the 5-inch weapons, may be feasible.

Partially assembled rounds are used for some 5-inch, 54-caliber guns and some 8-inch guns. With these rounds the projectile constitutes one package; the cartridge case containing the electrical igniter, main ignition charge, propulsion charge, wads, and plugs forms the complimentary package. The projectile with its explosive well sealed in steel may be expected to remain in good condition at great depths for long periods. It can be reused if not corroded and if the detonator assembly remains dry. The cartridge case, however, is more susceptible to wetting than is an assembled round. The end plugs (cork on old rounds, plastic on newer units) will yield at relatively low pressures, allowing water to enter the case. The immediate utility of the unit will be destroyed by the action of the water on the secondary igniter (black powder), and the propellant charge will deteriorate rapidly.

Unassembled rounds are used in some 8-inch weapons and in 12-inch and 16-inch guns. Projectiles are a separate package, as with partially assembled charges. The principal ignition system, which is loaded separately, is watertight but at moderate pressures may rupture, take on water, and be deactivated rapidly. Propellant is contained in cloth bags and is also loaded separately. The bags contain igniter charges and flashless pellets ( $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$ ) if required. The bagged propellant is stored in watertight containers but has no other protection. Once wet, igniters and flashless pellets leach rapidly and the propellant deteriorates over some 5 to 8 years. The propellant can be and has been salvaged and reworked. Rework is practical because usage is large, with about 740 pounds of propellant required for one firing of a 16-inch, 54-caliber gun.

### Rocket Motors

Solid propellant for rocket motors is either cartridge loaded or case bonded (cast in place). Mechanical property requirements for the two systems are quite different; case-bonded propellant is low-modulus material, whereas propellant for cartridge loads is high-strength, high-modulus material. It is relatively easy to remove a cartridge-loaded grain from the motor; it is only necessary to remove one end of the motor, release the pressure plate, and slide the propellant-and-inhibitor assembly out. Recovery of the propellant and hardware is therefore quite simple. Case-bonded propellant must be cut out with high-pressure water jets. It is practical to salvage hardware by this procedure, but the propellant and liner are irretrievably damaged.

Seals on rocket motors with solid propellants are adequate for protection against weather and normal hazards such as reduced pressure (air-launched missiles) or slightly elevated pressure as in a submarine. Most seals would fail, however, under hydrostatic pressure existing at moderate sea depths. Most propellants and igniters will be wetted and decomposition proceed as indicated in the various tables. When wet, igniters may fire but would probably fail to ignite the propulsion unit, since most of the heat would be dissipated by the seawater. The charge, however, could be ignited from an external source such as a cutting torch. Most units would not operate when wet, and performance would not be satisfactory after drying. Salvaged units, even those in advanced stages of corrosion and decomposition, can be identified by analysis with some accuracy. It is even possible to obtain significant information from burnt-out cases recovered from the sea.

Rockets fueled with binary liquids with each liquid stored in a separate tank are probably not more durable than solid propellant rockets. Failure would first be rupture of the tanks by pressure at moderate depths, with rapid dissipation of the fuel and oxidizer. Hypergolic or spark-ignited motors will not fire when significant amounts of water are present in the combustion chamber. In cases where tankage is sound and fuel delivery systems (pressurizing apparatus or pumps) intact, motors may be used after drying. These considerations also apply to liquid monopropellant and hybrid systems.

## CONCLUSIONS

The resistance of any specific article of ordnance to attack by seawater depends on the type of packaging and packing, structural strength of the assembly, materials of construction, rate of corrosion, tightness of seals, and susceptibility of the propellant, explosive, and associated devices to water damage.

Certain items such as mines, depth charges, and torpedoes are designed for undersea use and will remain intact and operative in seawater for long periods. They have been studied, and life expectancy under various conditions is known. Other items are intended for use in the atmosphere and are not fabricated to withstand ocean conditions. Of the items considered in this report, bombs are the most resistant to crushing or wetting, followed in order by projectiles, small-arms ammunition, small-caliber ammunition, small rockets, large rockets, and partially assembled ammunition.

When the contents of ordnance items remain dry, the salvaged piece may be identified and analyzed with great accuracy. It may be used after inspection in emergency conditions or used without inspection if failure to operate is an acceptable risk. It may be economically feasible to return such items to a central location, inspect them, and return serviceable units to current stockpiles.

It is quite probable, however, that essential parts will be wet by the seawater from leaking seals or crushing by hydrostatic pressure. If contents are wetted, the unit will become non-operative in a short time, but it may remain in a hazardous condition for long periods. Some materials, such as black powder, will be degraded in a matter of hours, but others will persist for years. The rate of degradation will depend on the chemical nature of the materials, water temperature, pressure, salinity, biological activity, and other factors. In most cases salvaged articles and contents can be identified, analyzed, and characterized to a large extent even after prolonged exposure to seawater.

Salvage for reclamation or rework poses other problems. In most instances such processes are not feasible or practical. Labor and hazards associated with recovery, shipping, unloading, and rework of small articles, even in large numbers, precludes such considerations. Large pieces usually contain advanced and complicated propellant and explosive formulations that would be difficult or impossible to rework to obtain reliable, high-performance products. In some cases recovery of large articles to obtain hardware or metals for reuse may be attempted, provided submersion time has been relatively short. In past efforts simple compositions in assembly containers such as single-base propellant in bags or canisters have been recovered, reworked, and used, but these operations cannot be considered as a model for future activities.

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13. ABSTRACT  Information is presented on the deterioration in sea water of materials and undersea-system components, based on published and unpublished studies, and on authoritative opinions. The items chosen for evaluation are primarily those likely to be used in deep-ocean structure and systems. Materials included are metals, plastics and composites, ceramics, paper, natural fibers; components included are photographic materials, magnetic tape, electronic components, and propellants and explosives. Marine corrosion of metals is represented in the form of an annotated bibliography; the remaining entries consist of summaries of material and component behavior coupled with pertinent bibliographies. The form and scope of these summaries run from comprehensive evaluations in the areas of plastics and propellants to relatively brief opinions of authorities for items of lesser marine utility or occurrence.			

14. KEY WORDS	LINK A		LINK B		LINK C	
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Electronic equipment						
Ceramic compounds						
Plastics						
Composite materials						
Reinforced plastics						
Polymeric films						
Fibers						
Fabrics						
Natural fibers						
Man-made fibers						
Synthetic fibers						
Rubbers						
Photographic materials						
Papers						
Paper products						
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Salvage						
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Rocket propellants						
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Rockets						