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TECHNICAL MEMORANDUM

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CORROSION AT 4500 FOOT DEPTH

IN

TONGUE-OF-THE-OCEAN

SR 004-03-01, Task 0589
Lab. Project 9400-72, Technical Memorandum 3

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SUMMARY

The Navy is increasingly involved with the corrosion and deterioration of materials to be used in the exploration of and operation in the deep ocean. A significant part of the corrosion and deterioration can be attributed to the action of microorganisms in the environment. The Naval Applied Science Laboratory has conducted exposures of a variety of metals (and organic materials) in the Tongue-of-the-Ocean at 4500-foot depth. These exposures served a threefold purpose: to provide needed general corrosion data for a variety of metals in the deep ocean; to facilitate acquiring corrosive microorganisms from corrosion products, sediment and water; and to provide corrosion data to be used in judging the reliability of corrosion rates obtained under deep-ocean simulated conditions in the Laboratory.

Recommendation is made for the study of deep ocean environmental influences on biological metabolism in relation to corrosion, and for the basic research of these influences on biological metabolism in relation to corrosion.

TABLE OF CONTENTS

ADMINISTRATIVE INFORMATION

Ref: (a) NAVAPLSCIENLAB Program Summary dated 1 Dec 1965, SR 004-03-01, Task 0589
(b) BUSHIPS ltr SR-004-03-01(00) Ser 1622B-77 of 25 Jan 1965
(c) NAVAPLSCIENLAB Project 9400-72, Technical Memorandum 1, Bibliography on Microbiological Corrosion: Deep Sea
(d) NAVAPLSCIENLAB Project 9400-72, Technical Memorandum 2, Microbiological Corrosion: Deep Sea
(e) BUSHIPS Journal. Undersea Material Exposures. Dec. 1965, pp 11-12
(f) Materials Protection. Corrosion of Metals in Tropical Environments - Aluminum and Magnesium. Dec. 1965, pp 30-35

1. In accordance with the objectives set forth in reference (a) and as authorized in reference (b), the U. S. Naval Applied Science Laboratory is conducting research on the corrosion and deterioration of materials by deep sea microorganisms leading to the development of preventive techniques. A comprehensive state-of-the-art study was completed and reported in reference (c). Experimental techniques and design of equipment for simulating the deep ocean biological and physical environment were reported in reference (d). This memorandum presents the results of corrosion exposure in the Tongue-of-the-Ocean, Bahamas for 3- and 6-month durations using a variety of materials.

ACKNOWLEDGMENTS

2. The work reported herein was conducted under the direction of W. L. Miller, Head, Inorganic Chemistry Branch. Assistance in making the exposures in Tongue-of-the-Ocean was provided by A. Anastasio of the Plastics and Elastomers Branch. The Bureau of Ships Program Manager is B. K. Couper, Code 1622B.

OBJECTIVE

3. The objective of this task is to determine the role of deep-sea microorganisms on the corrosion and deterioration of materials to be used in the deep ocean.

INTRODUCTION

4. This Laboratory is investigating the possibility of microbial corrosive and deteriorative mechanisms being operative under deep-ocean conditions which include high hydrostatic pressure, osmotic pressure and low temperatures. All of these physical factors are generally depressive to cellular activities,

with the possible exception of certain adapted organisms, and as such, may have significant effects on biological corrosive mechanisms. Research concerning these effects is required in view of the anticipated utilization of the ocean bottom in numerous applications including anti-submarine warfare. In situ testing of materials in the deep ocean has been undertaken in order to establish corrosion data under actual ocean conditions. These data will serve as criteria for judging experimental data in the laboratory under accelerated test conditions. They will also add to the store of information on the corrosion characteristics of a variety of metals for deep ocean use.

EXPERIMENTAL

5. The list of materials and experimental conditions of samples exposed in the Tongue-of-the-Ocean was given in reference (d). The total design of the corrosion array was presented in reference (e). Specimens were removed from the bottom corrosion rack after 3- and 6-month exposures. Immediately after removal, microbiological isolations were made from corrosion products. Specimens were washed with fresh water to remove sediment and sea water. After two such washes, they were rinsed with acetone and dried. Specimens were then sealed in polyethylene bags for shipment to the Laboratory. Color photographs of all samples were taken and are available for inspection at the Laboratory. Determination of corrosion rates and gross appearance of corrosion products and samples was performed in the laboratory. Corrosion products were removed by treatment of the samples in inhibited acid baths after degreasing with toluene and acetone. Uncorroded appropriate controls were simultaneously prepared to correct for the small amount of loss caused by the acid treatment. Specific acid treatments are listed in Appendix A in relation to metal types. After the corrosion product removal, specimens were washed free of acid, dried with acetone, heated at 240°C for 10 minutes to remove all absorbed water, and then weighed. Surface areas were determined. Data on corrosion weight loss and size for each sample were prepared for computer analysis and corrosion rates (inches per year) were calculated by the following general formula:

$$\text{Corrosion Rate (I.P.Y.)} = \frac{1}{\text{exposure (yrs.)}} \cdot \frac{\text{final volume}}{\text{final area}} \cdot \frac{\text{weight loss}}{\text{final weight}}$$

Corrosion rate for each sample and general observations of the type of corrosion are presented in Appendix B.

CONCLUSION

6. Comparison of the corrosion rates for each metallic specimen gives essential information concerning the durability of metals in a specific ocean bottom location. Metals can readily be arranged in order of durability by use of Appendix B. By comparison of the corrosion rates for

3-month and 6-month samples, the decrease in the corrosion rate after the 6-month exposure shows the tendency of various metals to passivate partially. This was also true of aluminum in galvanic couples with mild steel in which the progressive passivation of the aluminum reduced its corrosion rate and its galvanic protection of the steel. Only structural alloys of aluminum were used in the aluminum steel couples. It is possible that pure aluminum may not have become passivated. The effect of oxygen concentration cells is seen in the increased corrosion of aluminum and the decreased corrosion of mild steel (total specimen) resulting from the artificially created, partially anaerobic environment. Thus, the aerobicity of the local ocean bottom environment is an important parameter in metal durability, and the "zone of bottom influence" is significant. Aluminum 6061 was found to be the least corrosion resistant aluminum alloy and the corrosion data reported here for the deep ocean are consistent with those reported in reference (f) for shallow tropical ocean immersion.

FUTURE WORK

7. The Laboratory is continuing research on the effects of hydrostatic pressure on the metabolism of biological specimens. These include bacteria which were isolated from corrosion products, obtained from the specimens and from sediment and water from the exposure site. More detailed approach is being continued concerning protozoan metabolism under high hydrostatic pressure using artificial gas mixtures and synthetic nutrient medium. This will yield information concerning biological oxygen demand in the deep ocean and particularly the "zone of bottom influence." A report on this research will follow in April 1966. Estimation of the bacterial and chemical constituency of deep-ocean core samples (supplied by Lamont Geological Observatory) is being conducted. A report on this investigation is anticipated during May 1966.

RECOMMENDATIONS

8. Corrosion data obtained from specimens exposed in the deep ocean must be used as criteria for judgment of reliability of laboratory experiments. This is true not only for experiments dealing with electrochemical corrosion, but also for biological corrosion. On site deep ocean environmental parameters (high hydrostatic pressure, gas content, low temperature, dissolved materials, sediment type, and biological content) should be reproduced in laboratory deep-ocean corrosion research. Concerning biological corrosion, the two prime influences are hydrostatic pressure and low temperature.

APPENDIX A

REMOVAL OF CORROSION PRODUCTS

Metal Type	Treatment
Aluminum	Concentrated nitric acid in an ultrasonic bath at 25°C.
Mild Steel	10% hydrochloric acid by volume with 0.5% (by weight) 1,3-diethyl-2-thiourea in an ultrasonic bath at 25°C.
Monel (Alloy 400)	10% sulfuric acid by volume in an ultrasonic bath at 25°C.
Stainless Steel	30% nitric acid by volume in an ultrasonic bath at 25°C.
Lead, Chemical	Saturated ammonium acetate in an ultrasonic bath at 25°C.
Zirconium	Saturated ammonium acetate in an ultrasonic bath at 25°C.
Zinc	Saturated ammonium acetate in an ultrasonic bath at 25°C.
Titanium, Commercial RC-55	50% hydrochloric acid by volume in an ultrasonic bath at 25°C.
Copper	5% sulfuric acid by volume in an ultrasonic bath at 25°C.
Copper-Nickel Alloy (30% Ni)	10% sulfuric acid by volume in an ultrasonic bath at 25°C.
Nickel (200 "A")	10% sulfuric acid by volume in an ultrasonic bath at 25°C.

APPENDIX B

CORROSION RESULTS

Metal - Condition	Exposure (Months)	Figure*	Corrosion Rate (IPY)	General Observation After Removal from the Ocean Bottom
Aluminum 5086				
Plate	3	1,C	2.74×10^{-4}	No significant pitting
Plate	6	1,D	1.98×10^{-4}	No significant pitting
Aluminum 6061				
Plate	3	1,C	4.81×10^{-4}	Heavy pitting in localized areas.
Plate	6	1,D	5.49×10^{-4}	Very heavy and more frequent pitting in localized areas.
Aluminum 5052				
Plate	3	1,C	2.16×10^{-4}	No significant pitting
Plate	6	1,D	2.10×10^{-4}	No significant pitting
Aluminum 5456				
Plate	3	1,C	2.69×10^{-4}	No significant pitting
Plate	6	1,D	2.75×10^{-4}	Skin effect causing lamellar corrosion on edges.
Mild Steel				
Plate	3	1,C	6.00×10^{-3}	Generalized surface corrosion (iron oxide)
Plate	6	1,D	5.75×10^{-3}	Crevice Corrosion beneath Teflon spacer
Stainless Steel 304				
Disc	3	2,C	5.34×10^{-5}	No significant corrosion
Disc	6	2,D	1.15×10^{-5}	No significant corrosion
Copper				
Disc	3	2,C	1.26×10^{-3}	Red Corrosion Product (Cuprous oxide)
Disc	6	2,D	1.01×10^{-3}	Dark Red Corrosion Product (Cuprous oxide and Cupric oxide).

APPENDIX B

Metal - Condition	Exposure (Months)	Figure*	Corrosion Rate (IPY)	General Observation After Removal from the Ocean Bottom
Zirconium				
Disc	3	2,C	5.42×10^{-5}	No significant corrosion
Disc	6	2,D	2.05×10^{-5}	No significant corrosion
Titanium				
Disc	3	2,C	7.88×10^{-5}	No significant corrosion
Disc	6	2,D	2.14×10^{-5}	No significant corrosion
Magnesium				
Disc	3	2,C	40% weight loss	Extensive corrosion
Disc	6	2,D	80% weight loss	Extensive corrosion
Zinc				
Disc	3	2,C	2.72×10^{-3}	Extensive pitting concentrated beneath Teflon spacer
Disc	6	2,D	3.15×10^{-3}	Extensive pitting concentrated beneath Teflon spacer
Nickel				
Disc	3	2,C	5.23×10^{-5}	No significant corrosion
Disc	6	2,D	1.92×10^{-5}	No significant corrosion
Monel				
Disc	3	2,C	2.99×10^{-4}	Crevice Corrosion beneath Teflon spacer
Disc	6	2,D	2.83×10^{-4}	Crevice Corrosion beneath Teflon spacer
Tin				
Disc	3	2,C	--	Extensive pitting, crevice corrosion
Disc	6	2,D	--	Extensive pitting, crevice corrosion

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Metal - Condition	Exposure (Months)	Figure*	Corrosion Rate (IPY)	General Observation After Removal from the Ocean Bottom
Mild Steel				
Disc	3	2,C	4.49×10^{-3}	Generalized surface corrosion
Disc	6	2,D	7.89×10^{-3}	Crevice corrosion and surface corrosion
Lead				
Disc	3	2,C	3.52×10^{-4}	No sulfide coating
Disc	6	2,D	2.50×10^{-4}	No sulfide coating
Copper-Nickel				
Disc	3	2,C	3.18×10^{-4}	No significant corrosion
Disc	6	2,D	2.62×10^{-4}	Very slight local anodic corrosion
		Oxygen Concentration Cell Corrosion		
Mild Steel	3	3,C	4.78×10^{-3}	General Corrosion on Inner Face
Aluminum 5456	3	3,C	3.08×10^{-4}	Very slight Corrosion on Inner Face
Aluminum 5086	3	3,C	2.66×10^{-4}	Pitting beneath Nylon washers
Aluminum 6061	3	3,C	4.91×10^{-4}	Extensive pitting beneath Nylon washers
Aluminum 5052	3	3,C	3.71×10^{-4}	Slight crevice corrosion beneath Nylon washers
			Galvanic Couples	
Aluminum 5052) Aluminum 5456)	6	4	2.62×10^{-4} 4.05×10^{-4}	No significant corrosion Slight Pitting on inside face

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Metal - Condition	Exposure (Months)	Figure*	Corrosion Rate (IPY)	General Observation After Removal from the Ocean Bottom
			Galvanic Couples	
Aluminum 5052)	6	4	7.00×10^{-4}	Slight localized pitting on inside face
Aluminum 6061)			6.51×10^{-4}	General corrosion on inside face
Aluminum 5052)	6	4	1.33×10^{-4}	No significant corrosion
Aluminum 5086)			1.43×10^{-4}	
Aluminum 5456)	6	4	1.20×10^{-3}	Heavy pitting on inside face
Aluminum 6061)			5.34×10^{-4}	Heavy pitting on inside face
Aluminum 5086)	6	4	1.32×10^{-4}	No significant corrosion
Aluminum 5456)			1.46×10^{-4}	No significant corrosion
Aluminum 6061)	6	4	6.74×10^{-4}	Slight pitting on inside face
Aluminum 5086)			5.93×10^{-4}	Slight pitting on inside face
Aluminum 5052)	3	5	2.41×10^{-3}	Deep pitting beneath bolt heads; pitting
Mild Steel)			2.86×10^{-3}	Slight corrosion
Aluminum 5086)	3	5	3.15×10^{-3}	Very heavy pitting beneath bolt heads; along edges due to skin effect
Mild Steel)			2.19×10^{-3}	Slight corrosion
Aluminum 5456)	3	5	3.52×10^{-3}	Heavy pitting beneath bolt heads; severe edge corrosion due to skin effect
Mild Steel)			1.73×10^{-3}	Slight corrosion
Aluminum 6061)	3	5	3.25×10^{-3}	Deep pitting; severe edge corrosion due to skin effect
Mild Steel)			1.98×10^{-3}	Slight corrosion

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Metal - Condition	Exposure (Months)	Figure*	Corrosion Rate (IPY)	General Observation After Removal from the Ocean Bottom
Aluminum 5052)	6	6	1.26×10^{-3}	Extensive pitting beneath bolt heads
Mils Steel)			3.29×10^{-3}	Slight corrosion
Aluminum 5086)	6	6	2.22×10^{-3}	Extensive deep corrosion beneath bolts and along edges. Pitting on both surfaces.
Mild Steel)			2.69×10^{-3}	Slight corrosion
Aluminum 5456)	6	6	2.13×10^{-3}	Deep pitting beneath bolt heads; along edges.
Mild Steel)			2.46×10^{-3}	Slight corrosion
Aluminum 6061)	6	6	1.99×10^{-3}	Skin effect along edges; deep pitting
Mild Steel)			3.50×10^{-3}	Slight corrosion

* Code for Figures refers to color photographs available for inspection at the Applied Science Laboratory