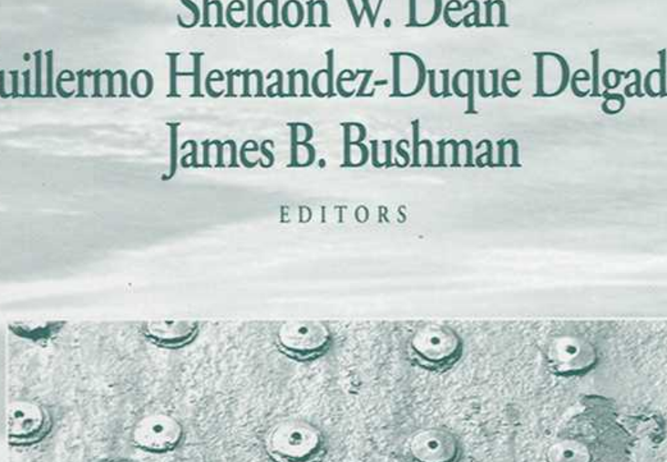
MARINE CORROSION in TROPICAL ENVIRONMENTS

Sheldon W. Dean
Guillermo Hernandez-Duque Delgadillo
James B. Bushman
EDITORS



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Foreword

This publication, *Marine Corrosion in Tropical Environments,* contains papers presented at the symposium of the same name held in Orlando, Florida, on 13 November 2000. The symposium was sponsored by ASTM Committee G01 on Corrosion of Metals, in cooperation with NACE International and the University of Mayab, Merida, Yucatan, Mexico. Sheldon W. Dean, Air Products and Chemicals, Inc., Guillermo Hernandez-Duque Delgadillo, Universidad del Mayab, and James B. Bushman, Bushman & Associates, presided as symposium chairmen and are editors of this publication.

Ann Chidester Van Orden
1954 to 1998

Dedication

This volume is dedicated as a memorial to our friend and colleague—Ann Chidester Van Orden, Professor, Old Dominion University, Norfolk, Virginia, who passed away on 14 October 1998.

Ann was a talented teacher, enthusiastic leader, and thorough researcher who gave tirelessly to those with whom she worked. She was a member of ASTM Committee G01 for years, and chaired the G01.99 standing subcommittee on Liaison with other Corrosion-related Organizations. She also was the vice chair for G01.11, subcommittee on Electrochemical Methods of Corrosion Testing and the task group on Electrochemical Corrosion Testing of Aluminum Alloys. She also was vice chair of the ASTM symposium on Electrochemical Modeling of Corrosion. Ann served on the ASTM Sam Tour Award Selection Committee. She was awarded the ASTM Committee G01 Certificate of Appreciation in 1993 for her many contributions to the committee and to electrochemical corrosion technology. Ann is a co-author of a paper in this STP.

Ann was also very active in NACE International, serving as vice chair for two symposia and chairing five others on a range of topics from the use of computers in corrosion control, electrochemical methods of corrosion testing, and atmospheric corrosion. Ann authored more than thirty technical papers and twelve technical reports. She supported two graduate student research projects and advised twenty undergraduate student research projects. She received the NBS Outstanding Performance Award in 1980, 1984, and 1986 and the NASA Special Accomplishment Award in 1992.

Beyond these and many other accomplishments, Ann was a very special person who brightened the lives of all whom she encountered. Her enthusiasm made difficult tasks easy and her joy in living shone through the most troubling times. Though she will be sorely missed as we move forward, the energy and creativity of her life will stand as a beacon illuminating our progress.

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Overview

Economic pressures on companies in the concluding decades of the 20th century have inspired a drive towards globalization. The need for continuing growth has pushed manufacturing, sales, and marketing beyond national boundaries to encompass all regions of the globe where populations present opportunities for these activities. One result of this initiative has been the economic development of tropical areas. Previously these areas were considered "third world" regions with little potential for growth. However, a number of factors have now combined to make these areas attractive for development. These include a more open political climate, discovery of oil and other natural resources, and improved transportation and communication means.

Tropical areas offer desirable climate, willing workers, and a large population with many needs and desires. The growth in industrialization has also promoted the development of infrastructures necessary to support this growth. Airports, marine terminals, power plants (hydroelectric, thermal, and nuclear), power distribution systems, water treatment plants and supply systems, highways, bridges, railroads, oil refineries, and chemical manufacturing facilities are some of the infrastructures which are required in most marine locations. As a result, atmospheric corrosion, concrete deterioration, and seawater corrosion are major concerns for infrastructures in tropical areas.

Papers were invited for this STP on atmospheric corrosion, corrosion of rebar in concrete, marine corrosion, and other related corrosion phenomena. It was intended that these papers would cover laboratory evaluation methods, test methods, and model prediction.

Atmospheric Corrosion

In the area of atmospheric corrosion, eight papers are included in this STP, covering a wide range of topics. M. Morcillo et al. have included summary results from sixteen tropical test sites participating in the "Ibero-American Map of Atmospheric Corrosiveness" (MICAT) project. This paper presents results from rural and marine locations without sulfur dioxide pollution and in marine sites with sulfur dioxide present. The four reference metals used were steel, zinc, copper, and aluminum exposed for one-year periods. Information is presented on the corrosion rate, corrosion products, and morphology of attack.

J. Tidblad et al. have analyzed data from the UN ECE and the ISO CORRAG programs and found that corrosion rates increased with ambient temperature up to 10°C and then decreased. They have created models for predicting the corrosion of steel, zinc, and copper as a function of time, temperature, relative humidity, sulfur dioxide, ozone, rainfall amount, and acidity. Different models are derived when chloride deposition occurs. These relationships are shown to give better predictions of corrosion than simple three variable expression.

I. S. Cole has analyzed data from five Pacific countries for steel and zinc. He has used regression analyses to develop model expressions for the corrosion rates of these metals as a function of time of wetness, acidity of precipitation, sulfur dioxide, and deposition of chlorides. In analyzing the atmospheric corrosion processes, he has examined both the absorption of acid gases in the moisture films and the deposition of aerosols from the atmosphere, including the effects of ammonia and the oxidation of sulfite to sulfate in corrosion product layers.

R. Klassen et al. have examined the corrosivity pattern near Townsville, Australia over a four-year period using the aluminum wire on copper bolt CLIMAT specimens and wet candle chloride collection units. The results showed that the corrosion rate of the specimen correlated with the chloride deposition measured by the wet candles. The authors used a computer fluid flow simulator to predict the effects of surface contours on the rate of salt deposition from marine surf generated aerosols. The predictions provided a framework for understanding the unusual pattern of salt deposition and resulting corrosivity.

B. S. Phull et al. have presented a summary of their 38 years of atmospheric corrosivity monitoring at the Kure Beach sites. They have used two reference materials, steel and zinc, in this work while also monitoring chloride deposition, relative humidity, time of wetness, temperature, prevailing wind direction, and rainfall. One important conclusion from their work is that violent hurricanes do not have a significant effect on the one-year corrosion losses but can cause mechanical damage and loss of specimens. They have concluded that actual exposure data is the best indication of a material's performance in the atmosphere.

D. C. Cook et al. have examined results for twelve sites located around the Gulf of Mexico. One-year exposures of steel, aluminum, copper, and zinc were used along with measurements of time of wetness, chloride deposition, and sulfur dioxide concentrations. They have evaluated the estimated corrosivity classes based on the ISO 9223 method and compared it with the class obtained by mass loss measurements. They found substantial disagreements between corrosion classification based on environmental parameters and specimen losses. They have also provided some detailed analyses of the rust layer found on the carbon steel panels.

J. Uruchurtu-Chavarín et al. have looked at a variety of electrochemical techniques including linear polarization resistance and electrochemical potential noise to evaluate the protectiveness of rust layers on carbon steel specimens exposed as part of the MICAT program. These measurements were able to provide a measure of protectiveness of the rust layers, including the observation that low levels of sulfur dioxide improved the protectiveness of the rust. Low levels of chloride deposition reduced the protectiveness of the rust but sulfur dioxide was still beneficial. Extreme levels of chloride and sulfur dioxide were very detrimental.

G. A. King and P. Norberg have developed an approach for evaluating fabricated metal products in marine atmospheres. They have specifically addressed the issue of sheltering which greatly aggravates the damage in marine sites because rain is not able to wash chloride from the surfaces. They considered a variety of coatings on sheet steels including zinc, 5% Al zinc, 55% Al zinc, sheet aluminum, and sheet stainless steel. Specimens with organic coatings were included as well. These specimens included a variety of defects such as cut edges, bends, domes, scribes, and holes. A system of evaluating and rating damage was developed. Exposures were made at three marine sites. Comparisons were presented for open versus sheltered locations.

Concrete Deterioration

Nine papers on various aspects of concrete deterioration are included. A. T. C. Gumarães and P. R. L. Helene have examined the issue of chloride diffusion in hydrated and cured portland cement paste. They applied a chloride-containing mixture to the surface of their specimens and observed the degree of penetration of chloride into the specimens as a function of degree of saturation of the specimens with water. They concluded the diffusion of chloride into the concrete was strongly influenced by degree of saturation, and this effect should be taken into consideration in evaluations.

L. Maldonado has studied the electrical conductivity of concrete and mortars as a function of water to cement ratio and curing times of 7 and 28 days. Specimens were immersed in a solution of 1, 2, 3, and 4M sodium chloride, and the conductivity of the specimens was measured. It was found that the conductivity increased with salt concentration and water content of the mixture. The mortars cured for 28 days had higher conductivities than those cured for 7 days, while the concrete specimen showed lower conductivity with longer cure times. This behavior was explained by the difficulty of water transport in the gel pore structure.

P. Castro and L. P. Véleva have examined the issue of internal relative humidity in concrete during settling, curing, and service. They have conducted experiments using the ASTM G 84 Cu/Au wetness sensor at various depths in concrete specimens to trace moisture levels high enough to produce wetness response on the sensor. They have examined diurnal temperature variations and found corresponding time of wetness variations corresponding to the temperature changes. They have proposed this approach for understanding why concrete structures show variations in deterioration from rebar corrosion.

L. P. Véleva and M. C. Cebada have examined the use of saturated calcium hydroxide solutions as compared with pore solutions from concrete to model the corrosion of rebar from chloride intrusion. They noted significant differences in the electrochemical responses of steel in those solutions using both potentiodynamic polarization and electrochemical impedance spectroscopy. They concluded that the concrete pore solution was somewhat more protective than the saturated calcium hydroxide.

R. de Gutiérrez et al. have examined the properties of cement mortar blended with silica fume, fly ash, and blast furnace slag. They have run tests on compressive strength, water absorption, chloride diffusion and permeability, mercury intrusion, and x-ray defraction. The densifying effects of these materials improved the resistance of concrete to chloride intrusion although the fly ash and slag additions lowered early strengths more than silica fume.

R. de Gutiérrez et al. have investigated the use of a variety of fiber materials to improve the ductility and tensile strength of concrete mortar. They included both natural and synthetic fibers in this study. Silica fume and superplasticizer were added to some of the mixtures. The durability of the various mixtures was evaluated by measuring chloride penetration and water absorption. The compressive strength was also measured. It was found that all the fibers reduced the compressive strength of the mortars with steel showing the smallest reduction and sisal the greatest. The addition of silica fume improved the compressive strength after 90 days curing so that mortars with steel, glass, and coconut fibers had greater strength than mortar without fibers. Likewise, water absorption was greatest for sisal and fique and smallest for steel and polypropylene. Addition of silica fume and superplasticizer reduced the water absorption in all cases. Chloride penetration was also reduced when silica fume was used.

Another approach to dealing with the problem of rebar corrosion in concrete was presented by J. L. Piazza II. He has reviewed a number of approaches for dealing with both preventing corrosion of rebar from chloride intrusion and remediation of damage. He has focused his discussion on the use of zinc hydrogel anodes as a low maintenance cathodic protection system for concrete buildings in tropical marine environments. This approach is particularly desirable for existing structures that are showing the effects of chloride intrusion and rebar corrosion.

Z. Chaudhary presented his experience with cathodic protection systems for seawater intake structures in petrochemical plants in Saudi Arabia. Seawater is used here for cooling and, as a result, there are extensive canals and distributions systems. Both impressed current and sacrificial anode galvanic systems were used to provide protection for the rebar in these concrete structures. The design philosophy is covered together with monitoring, repair, and performance evaluations over a seven-year period. Recommendations are provided for the applied current density and protection potential criterion for these structures. He also recommends that impressed current systems should be included in the design of new units.

L. Tula and P. R. L. Helene have examined the possibility of using Type 316L stainless steel rebar rather than carbon steel to avoid concrete failures from rebar corrosion. They examined polarization curves of these metals in concrete with various chloride contents and determined that carbon steel would have about 10 times greater corrosion rate at a chloride content greater than 0.4%. They also examined the extent of corrosion required to achieve loss of bond strength and cracking of the concrete. The stainless required a somewhat greater extent of corrosion to lose bond strength in the concrete but somewhat smaller extent of corrosion to cause cracking of the concrete. The stainless steel showed substantially greater strength at equivalent weight loss values. Calculations were made on the expected service lives for a marine pier and an industrial chloride solution reservoir for stainless steel as compared to carbon steel rebar. The results varied from two to eight times for stainless steel greater than carbon steel.

Cathodic Protection Microbiological Influenced Corrosion and Seawater

Four papers are included in this section. E. W. Dreyman has considered the unique challenge presented by the need to place metal items in coral sands with seawater present. This includes items such as water and gas lines and tanks to hold water, fuel, and other fluids. The challenge here is to establish protection criteria for steel and aluminum construction in this service. He covers rectifiers, cables, and galvanic and impressed current anodes. He also provides information on monitoring and design parameters for this type of condition.

B. J. Little et al. have examined fungi growing inside aircraft operating in tropical marine environments. These organisms grow on painted and bare surfaces particularly in occluded areas where cleaning is difficult. The high humidity of tropical environments encourages fungal growth. Fungal growth can cause paint deterioration and corrosion attack on aluminum surfaces. Cultures taken from aircraft were grown on a variety of surfaces including bare aluminum, glossy polyurethane coated surfaces, and flat finish polyurethane coated surfaces both with and without fungicide and fungistat additives. The flat finish was somewhat better than glossy finishes. Aged paint fouled more rapidly than new coatings and the additives produced mixed results.

H. A. Videla et al. have analyzed the action of sulfate-reducing bacteria (SRB) on the corrosion of carbon steel in seawater and marine mud. They have noted that SRB cause a variety of changes to pH, ion concentrations, and corrosion product films with results of acceleration of corrosion and related problems such as corrosion fatigue, crack growth, and hydrogen embrittlement. The presence of SRB can also decrease the performance of cathodic protection and protective coatings used in seawater. A review of electrochemical techniques for corrosion assessment, surface analyses, and microscopy methods is also provided.

R. M. Kain has evaluated epoxy coatings for protecting Type 316L stainless steel, 6Mo stainless steel (N08367), and a CrNiMnMo stainless steel. A variety of different specimens was exposed to warm filtered seawater in a large tank for 6 months. The results showed that all the specimens suffered crevice corrosion and paint delamination. Grit-blasted surfaces had much better paint adhesion. The 6Mo stainless steel gave the best performance but was not immune to crevice attack. This work demonstrated the effectiveness of epoxy coatings as crevice formers in seawater.

This book should be of particular interest to engineers responsible for designing and maintaining protection programs for physical plants in tropical marine locations. In addition, many of the papers present models and data that are of specific interest to scientists studying degradation mechanisms that occur in natural environments. Some of the papers are of specific interest to researchers developing new products for use in these environments. Also, these papers have many important insights for standards' developers, especially those interested in standards with global reach. In particular, these papers will be of interest to standards' developers concerned with corrosion resistant alloys, coatings and linings, cathodic protection, concrete, seawater, and atmospheric corrosion.

The editors of this book are especially grateful to Victor Chaker for his efforts in organizing this activity. Victor's visions and enthusiasm were responsible for the concept and initial plans. Unfortunately Victor had to withdraw from this project due to his personal situation, but his contributions are recognized and much appreciated.

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