Degradation of Metals in the Atmosphere









DEGRADATION OF METALS IN THE ATMOSPHERE

A symposium sponsored by ASTM Committee G-1 on Corrosion of Metals Philadelphia, PA, 12–13 May 1986

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FOREWORD

The Symposium on Degradation of Metals in the Atmosphere was presented at Philadelphia, PA, on 12-13 May 1986. The symposium was sponsored by ASTM Committee G-1 on Corrosion of Metals. Sheldon W. Dean, Air Products and Chemicals, Inc., and T. S. Lee, National Association of Corrosion Engineers, served as chairmen of the symposium and are editors of the resulting publication.

Related ASTM Publications

Atmospheric Corrosion of Metals, STP 767 (1982), 04-767000-27

Atmospheric Factors Affecting the Corrosion of Engineering Metals, STP 646 (1978), 04-646000-27

Corrosion in Natural Environments, STP 558 (1974), 04-558000-27

A Note of Appreciation to Reviewers

The quality of the papers that appear in this publication reflects not only the obvious efforts of the authors but also the unheralded, though essential, work of the reviewers. On behalf of ASTM we acknowledge with appreciation their dedication to high professional standards and their sacrifice of time and effort.

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Introduction

ASTM has provided leadership in generating information on atmospheric corrosion since 1906 when the first ASTM exposure program was initiated. Much of the early test work was aimed at evaluating the effective life of protective coatings so that meaningful specifications could be written. In 1964, Committee G-1 on the Corrosion of Metals was formed, and its scope included "the promotion and stimulation of research" and "collection of engineering data relating to the corrosion of metals." Subcommittee G01.04 on Atmospheric Corrosion has pursued these goals through a series of symposia that have resulted in Special Technical Publications (STPs).

The first of these symposia was held in Boston, MA, 25-30 June 1967 and resulted in ASTM STP 435 [1]. The next symposium was held in Philadelphia, PA, 24-29 June 1973, and the papers were published in STP 558 [2], together with the papers of two other symposia. The Golden Anniversary Symposium commemorating 50 years Atmospheric Exposure Testing at the State College Rural Test Site was held at Pennsylvania State University, State College, PA, 18-19 May 1976, and the papers were published in STP 646 [3]. The Symposium on Atmospheric Corrosion of Metals was held in Denver, CO, 19-20 May 1980 and resulted in STP 767 [4]. The approach of using symposia has allowed wide participation and more comprehensive coverage of the subject. Contributions from sources outside the United States have also given these publications an international scope.

The Symposium on Degradation of Metals in the Atmosphere was organized as a continuation of the atmospheric corrosion series. The following goals were identified for the symposium:

• to highlight the performance of new alloys and metallic combinations, including metallic coatings,

• to report on the behavior of metals and alloys used in atmospheric service,

• to provide updated information on the effects of sulfur oxides and other accelerators of atmospheric corrosion,

• to report on studies showing correlation between atmospheric exposure results and laboratory tests designed to simulate atmospheric service, and

• to discuss the development and use of standards to control and minimize the atmospheric corrosion of metals.

The atmosphere has undergone significant changes in the past two decades in the United States. The efforts to reduce air pollution levels have resulted in significant reductions in ground level sulfur dioxide concentration, together with reduced lead content in particulates near highways. However, the use of tall stacks on coal fired electric power generating facilities has created widespread concerns about acid precipitation. Increased usage of deicing salts to maintain ice and snow-free thoroughfares have also increased the prevalence of chlorides in nonmarine environments. The development of atmospheric monitoring systems and the widespread availability of computers have made possible extensive modeling and correlation studies. All of these developments have made the study of atmospheric corrosion a dynamic and challenging field in spite of eight decades of work.

The symposium that was held 12-14 May 1986 in Philadelphia featured 30 speakers on a wide variety of topics. All the major engineering metals were covered, including weathering and structural steel, stainless steels, zinc galvanized steel, aluminum and copper alloys. Several

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other papers on atmospheric effects, corrosion monitoring, clad metals, and computer modeling rounded out the program.

In 1976, the first plenary meeting of the International Organization for Standardization (ISO) Technical Committee 156 in Corrosion of Metals and Alloys met and identified atmospheric corrosion as a priority area for standards development. Two working groups were formed to address aspects of atmospheric corrosion. Working Group 3 (ISO/TC 156/WG3) was concerned with corrosion test methods, while Working Group 4 (ISO/TC 156/WG4) was concerned with classification of atmospheric corrosivity. Working Group 4 is now sponsoring an atmospheric exposure program that is described in this STP.

In view of the wide coverage and international participation in this symposium, this STP provides a cross section of the state of the art in atmospheric corrosion testing in the mid 1980s. Taken with the other ASTM STPs, it provides a comprehensive view of the subject. However, the field is continuing to develop and more symposia will be needed in the future.

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C. R. Shastry, ¹J. J. Friel, ² and H. E. Townsend¹

Sixteen-Year Atmospheric Corrosion Performance of Weathering Steels in Marine, Rural, and Industrial Environments

REFERENCE: Shastry, C. R., Friel, J. J., and Townsend, H. E., "Sixteen-Year Atmospheric Corrosion Performance of Weathering Steels in Marine, Rural, and Industrial Environments," *Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 5-15.

ABSTRACT: Weathering steels ASTM A 242-Type 1 and ASTM A 588-Grade B and steels with 0.21 and 0.021% copper are tested for atmospheric corrosion resistance in marine, rural, and industrial environments. The 16-year atmospheric exposure test results obey well the kinetic equations of the form $C = At^B$, where C is the corrosion loss, t is time, and A and B are constants. The corrosion resistance of steels is compared on the basis of times required to achieve a 250 μ m thickness loss calculated using the rate equations. In these environments, weathering steel ASTM A 242 is at least 16 times more corrosion resistant than the 0.021% copper steel and at least four times more durable than the 0.21% copper steel and at least two times more durable than the 0

KEY WORDS: corrosion, corrosion tests, atmospheric corrosion, industrial environment, marine environment, rural environment, steels, weathering steel, kinetics, regression analysis

Atmospheric corrosion can lead to the deterioration of steel structures. Although the effects of corrosion can be reduced by painting, it is often more advantageous to make use of maintenance-free weathering steels. The term weathering steel applies to a class of low-alloy steels that contain small amounts of such alloying elements as Cu, Cr, Ni, P and Si, which promote the formation of a protective rust layer that acts as a self-healing barrier against further corrosion. The attractive and protective rust layers that develop on these steels during outdoor exposure, coupled with no need for maintenance, have provided the necessary impetus for the widespread use of weathering steels over the years in a variety of structural applications including buildings and bridges.

The weathering steels are covered by ASTM Specification (A 588-77a, Grade B) for highstrength low-alloy structural steel with 345 MPa (50,000 psi) minimum yield strength to 102 mm thick and by Specification (A 242-75, Type 1) for high strength low-alloy structural steel. Bethlehem produces both of these grades under the trade names Mayari R-50 and Mayari R, respectively. The main difference between the two grades is in their P content, which in the case of A 242 is about 0.10%, whereas for the A 588 steel it is held below 0.04% for improved tough-

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ness and weldability. The complete analysis of the two Bethlehem grades is given in Table 1 along with the corresponding ASTM specifications. The revised A 588 Specification (A 588-82, Grade B) has a higher upper limit for Si than the earlier (A 588-77a, Grade B) version (0.50% versus 0.30%). This change was made in order to further enhance the corrosion resistance of this steel based on published information on the effect of Si [1]. It is expected that the atmospheric corrosion performance of the new grade (A 588-82, Grade B) will be better than that of the earlier (A 588-77a, Grade B).

Atmospheric corrosion performance of weathering steels is usually measured in terms of thickness loss over a period of time. In an earlier paper [2], the eight-year atmospheric corrosion performance of A 588 weathering steel in industrial, rural, and marine environments was described. It was shown that the atmospheric corrosion performance of A 588-77a, Grade B exceeds the ASTM specification that the weathering steel be two times more durable than carbon structural steel with copper (0.20 minimum-percent Cu), and four times more durable than carbon structural steel without copper (0.02 maximum-percent Cu).

We have now obtained 16-year atmospheric exposure test results which lend further support to the above conclusion. Additionally, we have also obtained long-term atmospheric exposure test results for the A 242-75, Type 1 weathering steel, which indicate an outstanding corrosion performance by this steel in all three types of test environments. This paper presents the results of 16-year outdoor corrosion tests on the two weathering steels (A 588-77a, Grade B and A 242-75 Type 1) in three different environments and compares their performance with that of carbon structural steels both with and without copper.

Materials and Test Procedures

The composition of steels tested is given in Table 1. Plant-produced 38-mm thick weathering steel plates are hot-rolled in our laboratories to 2.5-mm thickness, and from these sheets, panels measuring approximately 150 mm \times 100 mm \times 2.5 mm (6 in. \times 4 in. \times 0.1 in.) are cut, grit-blasted, stamped with identification, degreased, and weighed before atmospheric exposure.

The steel containing 0.21% copper is similarly prepared from 5 mm plate. The steel with 0.021% copper is procured in the form of cold-rolled and annealed 2.8-mm (0.11 in.) carbon steel sheet. The latter steel is similar to that used by Coburn et al. [3] in an ASTM study to determine the severity of various atmospheric test sites.

The test panels are exposed 30° from the horizontal, with skyward surfaces facing south at three test sites (described below) representing a broad range of environmental conditions:

1. Kure Beach, NC: This is an internationally known marine test site located about 250 m from the open Atlantic Ocean, and is operated by the LaQue Center for Corrosion Technology.

2. Saylorsburg, PA: This site is located in the Pocono Mountains about 50 km north of Bethlehem. The site is operated by Bethlehem Steel.

3. Bethlehem, PA: This is an industrial site in the proximity (3 km) of Bethlehem Steel's integrated steel making facility.

A comparison of these sites over the years 1968 to 1984 is given in Fig. 1. This figure shows the corrosion loss of 1.2-mm, thick-rolled pure zinc panels (Zn \geq 99.85%, Pb = 0.09%, Al < 0.005%, Cu < 0.005%, Cd < 0.01%, Mg < 0.005%, Sn < 0.005%, Fe = 0.02%) exposed as controls at the same time as the test specimens. The zinc corrosion rate averaged 1.64 μ m/year at the Saylorsburg site, 1.91 μ m/year at Bethlehem, and 2.12 μ m/year at Kure Beach.

Exposed duplicate specimens were removed after one, two, six, eight, and 16 years of exposure, cleaned in a molten sodium hydroxide (NaOH)-sodium hydride (NaH) mixture to remove corrosion products, and reweighed to determine metal loss according to ASTM Recommended Practice G 1-81. Details of the sodium hydride cleaning process are given in Du Pont publication SP 29-370 [4]. Briefly, our procedure consists of immersing preheated weathered steel panels in a carrier bath of fused NaOH containing about 2% NaH at a temperature of 643 K \pm 10.

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1-Composition
TABLE

				Comp	osition, % by V	Veight			I
Steel	C	Mn	d	s	Si	ïZ	ర	C	>
ASTM Specification A 242-75. Type 1	0.15 max	1.00 max	0.15 max	0.05 max	:	÷	÷	0.20 min	•
A 242 Test Material	60.0	0.65	0.11	0.032	0.29	0.66	0.52	0.27	:
ASTM Specification: A 588-82. Grade B	0.20 max	0.75-1.35	0.04 max	0.05 max	0.15-0.50	0.50 max	0.40-0.70	0.20-0.40	0.01-0.10
ASTM Specification A 588-77a, Grade B	0.20 max	0.75-1.25	0.04 max	0.05 max	0.15-0.30	0.50 max	0.40-0.70	0.20-0.40	0.01-0.10
A 588 Test Material	0.13	1.02	0.008	0.018	0.22	0.27	0.64	0.21	0.062
0.21 Cu Test Material	0.02	0.35	0.005	0.013	0.01	0.02	0.02	0.21	:
0.021 Cu Test Material	0.07	0.35	0.009	0.020	< 0.001	0.01	0.02	0.021	: : :



FIG. 1-Corrosion of pure zinc from 1968 to 1984 at each site.

Sodium hydride, the active descaling agent, is generated in the bath by reacting metallic Na and H in generators that are partially immersed in the fused hydroxide bath. The time of immersion is approximately 20 min. Following immersion, the panels are removed from the bath, allowed to drain for a short time, and then quenched in water, scrubbed, and allowed to dry before weighing.

Results and Discussion

Results of the corrosion tests are plotted as a linear function of time in Figs. 2 to 4. Each point in these figures represents the average of the corrosion loss values from duplicate specimens. The individual values for the duplicate specimens differ in general by less than 5% of the average value. On the basis of these data, the steels can be qualitatively ranked in terms of their corrosion resistance as follows: A 242 weathering steel > A 588 weathering steel > 0.21 Cu steel > 0.021 Cu steel. When replotted on logarithmic scales, Figs. 5 to 7, the same data fit well to straight lines. These straight line relationships can be represented by equations of the form shown below:

$$\log C = \log A + B \log t \tag{1}$$

where

C = corrosion loss in micrometers, t = time in years, and A and B = constants.

The constants of the equation are obtained by linear regression analysis of these data, and are shown in Table 2 along with the associated correlation coefficients, R. The R values listed in the



FIG. 2-Corrosion performance of steels at Kure Beach, NC.



FIG. 3-Corrosion performance of steels at Saylorsburg, PA.



FIG. 4—Corrosion performance of steels at Bethlehem, PA.



FIG. 5-Logarithmic plot of corrosion performance at Kure Beach, NC.



FIG. 6-Logarithmic plot of corrosion performance at Saylorsburg, PA.



FIG. 7-Logarithmic plot of corrosion performance at Bethlehem, PA.

	We	atherin ASTN 242-Ty	ig Steel 1 A pe 1	We 5	atherin ASTN 588-Gra	ig Steel I A ide B	0).21 Cu	steel	0	.021 Cu	ı steel
Test Site	A ^a	Bª	R ^b	A	В	R	A	В	R	A	В	R
Kure Beach, NC Saylorsburg, PA Bethlehem, PA	23 21 32	0.57 0.36 0.20	0.991 0.994 0.999	28 29 42	0.63 0.42 0.31	0.998 0.994 0.977	30 29 48	0.76 0.57 0.37	0.999 0.997 0.996	32 33 76	1.44 0.65 0.32	0.990 0.996 0.997

TABLE 2-Regression coefficients for 16-year atmospheric corrosion data.

"A and B are coefficients of the equation $C = At^{B}$, where C is the corrosion loss in micrometers and t the exposure in years.

 ${}^{b}R$ is the correlation coefficient of the least-square regression of the logarithms.

table are 0.990 or greater in all cases except one, indicating that 98% (R^2) of the changes with time are accounted for by the rate equations.

To make quantitative comparisons of the corrosion resistance of steels, Eq 1 should be put in the exponential form by taking antilogarithms of the terms

$$C = At^B \tag{2}$$

From Eq 2, Townsend and Zoccola [5] developed relationships to quantitatively compare the corrosion resistance of steels on the basis of corrosion loss after a fixed time of exposure, corrosion rates after a given period of exposure, and ratio of times required to achieve a particular thickness loss. They showed that the first two criteria understate the advantages of most corrosion resistant materials in the less-corrosive environments within the time period of typical corrosion tests, whereas the last criterion provides a more satisfactory basis for comparison. The selection of loss of thickness for computation of the ratio of times should, however, meet the following requirements:

1. The loss should be large enough to distinguish differences between materials.

2. The loss should not be so large that even the least corrosion-resistant material cannot achieve it within a reasonably short time.

3. The loss should be within the design allowances. That is, the loss should result in an insignificant reduction in load-bearing cross-sectional area.

Based on these considerations, Townsend and Zoccola [2] select a loss of $250 \,\mu m \,(0.01 \text{ in.})$ for the calculation of time ratios. The times to exhibit a 250 μm thickness loss are calculated by solving Eq 2 for time

$$t^* = \left[\frac{C^*}{A}\right]^{1/B} \tag{3}$$

where

 $t^* = \text{time in years to achieve 250 } \mu \text{m corrosion loss},$

 $C^* = \text{corrosion loss selected (250 } \mu\text{m}), \text{ and}$

A and B = constants of the rate equation (see Table 2).

The same considerations can be used to specify a loss of thickness appropriate to each situation. The time to achieve a specified thickness loss thus provides a general basis for comparing

		A T		unhai aun		NCZ IN SON SON	, μm.		
		Time, years	1				Ratio of Times		
Test Site	Weathering, A 242-Type I	Weathering, A 588-Grade B	0.21 Cu	0.021 Cu	A 242-Type 1: 0.21 Cu steel	A 242-Type 1: 0.021 Cu steel	A 588-Grade B: 0.21 Cu steel	A 588-Grade B: 0.021 Cu steel	0.21 Cu steel: 0.021 Cu steel
Kure Beach, NC	65.8	32.3	16.3	4.2	4.0	15.7	2.0	7.7	3.9
Saylorsburg, PA	673	169	43.8	22.2	22.0	43.8	3.9	7.6	2.0
Bethlehem, PA	29100	316	86.5	41.3	336	705	3.7	7.7	2.1

020

the atmospheric corrosion performance of weathering steels. This is especially significant considering that no standard criteria are available in current ASTM specifications for comparing the corrosion resistance of various weathering steels.

The times required to achieve $250 \cdot \mu m$ corrosion loss and the ratio of times for the various steels are shown in Table 3. The table shows that time ratios calculated for 0.21 Cu steel relative to 0.021 Cu steel fall in the 2.0 to 3.9 range. This result thus conforms to the ASTM specification that copper bearing steel have approximately twice the corrosion resistance of structural steel without copper.

The time ratios for ASTM A 242 in Table 3 indicate that this weathering steel is 16 to over 700 times more durable than the 0.021 Cu steel and four to 336 times more durable than the 0.21 Cu steel with the greatest relative durability occurring in the industrial environment. ASTM A 588 weathering steel is about eight times more corrosion resistant than the 0.021 Cu steel and two to four times more corrosion resistant than the 0.21 Cu steel.

Table 3 also shows that the Kure Beach, NC test site has the most severe environment in terms of long-term corrosivity. Saylorsburg, PA ranks next followed by the Bethlehem, PA site, which is the least corrosive to these steels.

On the basis of 16-year data, the times required to reach a thickness loss of 1250 μ m are consistently higher for all the steel grades in Saylorsburg and Bethlehem compared to the times previously predicted from eight-year data [2]. This result is interpreted as indicative of a significant improvement in the environmental quality in the past eight years at Saylorsburg and Bethlehem. The improvement may, in part, be attributed to the cessation of operation of a zinc smelter located 25 km west of Saylorsburg, and to the stringent pollution control measures that are in effect at the Bethlehem steel plant in Bethlehem. These results are in general agreement with the results of a separate study [5] in which it was shown that the long-term corrosivity of Bethlehem and Saylorsburg environments relative to zinc coated and an aluminum-zinc alloycoated steel decreased in the period from 1964 to 1981. It was also shown in the study that during the same period the corrosivity of the Kure Beach environment also decreased for coated steel. The present work, on the other hand, shows that no significant change has occurred in the corrosivity of the marine environment as it relates to weathering steels since identical times to achieve the 250-µm thickness loss are predicted on the basis of the 16-year exposure data and the earlier eight-year data. It is possible that the reported increase in corrosivity of the Kure Beach site in the past few years³ has offset the decrease in corrosivity experienced in the previous years. The net result of the two opposing trends would be to leave the corrosivity of the marine environment essentially unchanged, as observed.

Conclusions

The main conclusions from an analysis of 16-year atmospheric corrosion test data for A 242-Type 1 and A 588-Grade B weathering steels, 0.21 Cu steel, and 0.021 Cu steel are as follows:

1. These steels can be ranked in order of decreasing atmospheric corrosion resistance as: A 242 weathering steel > A 588 weathering steel > 0.21 Cu steel > 0.021 Cu steel.

2. On the basis of calculated ratios of times to exhibit a $250 \mu m$ corrosion loss, A 242 weathering steel is 16 to 700 times more corrosion resistant than the 0.021% copper steel and four to 336 times more corrosion resistant than the 0.21% copper steel. On the same basis, weathering steel A 588 is seven to eight times more durable than the 0.021% copper steel and two to four times more durable than the 0.21% copper steel.

3. Sixteen-year atmospheric corrosion behavior of the above steels in industrial, rural, and marine environments is well represented by exponential rate equations readily derived by regression analyses of the data expressed in logarithmic form. Eight-year data provide an equally accurate prediction of corrosion at Kure Beach but give conservative predictions at Bethlehem or Saylorsburg.

Acknowledgments

The authors are indebted to E. L. Gehman for technical assistance in conducting the tests.

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DISCUSSION

¹P. Albrecht (discussion question)—You have mentioned that the chemical composition of Mayari-R 50 was changed in 1977. Can you, please, explain why it was found necessary to change the chemical composition?

C. R. Shastry, J. J. Friel, and H. E. Townsend (authors' closure)—As indicated in the text, this change was made to further enhance the corrosion resistance of this steel, based on published information on the beneficial effect of silicon [1].

Atmospheric Corrosion Problems with Weathering Steels in Louisiana Bridges

REFERENCE: Raman, A., "Atmospheric Corrosion Problems with Weathering Steels in Louisiana Bridges," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 16-29.

ABSTRACT: ASTM A-588 weathering steels, grades A and B, used in bridge structures in the United States and abroad, are not as immune to atmospheric corrosion as originally predicted. Under dry conditions and wet and dry cycles of nearly equal length, the steel forms a protective rust layer and corrodes the least. However, under wetter conditions and in the presence of stagnant water, more rusting and the formation of nonprotective rust layers are found. The presence of chloride as well as other acid-forming pollutants in the atmosphere enhances corrosion. The rust layer forms coarse flakes, which lose adherence and protectiveness. Excessive flaking and a greater-than-expected loss of section thickness result. The presence of salt and high humidity, favorable for water condensation, promotes pitting under the flakes and sheets of rust. The rust develops in the form of small mounds and grows stepwise in layers, with the iron for the growth of the rust mound obtained from the metal underneath these mounds. Because of this, wide pits develop under the mounds and corrosion proceeds by the differential aeration cell mechanism. In areas where water stagnates, rusting occurs over the entire surface and a continuous rust layer develops from a sedimentary deposit. The presence of chloride and soluble salts derived from atmospheric contaminants promotes corrosion by not only increasing the conductivity of the condensed water, but by reducing the availability of oxygen at the corroding anodic sites as well.

KEY WORDS: weathering steels, atmospheric corrosion problems, flaking, pitting, chloride effects, mechanism of pitting, differential aeration cells, exterior and interior locations in bridges

ASTM A-588 weathering steels, grades A and B, have been used widely in the last two decades to build bridges in the United States and all over the world. About 2240 such bridges are in use in the United States and two Canadian Provinces [1]. Tests undertaken in the field as well as in laboratories indicated that these steels form a uniform and adherent protective rust layer as they weather in the atmosphere and, hence, would not require painting or any other form of protection. In practice, though, this is not the case. Sections of these steels form protective rust only when used under dry weather conditions or in wet-dry cycles of nearly equal lengths. However, under wetter conditions in the presence of high humidity and chloride or when water remains stagnant on their surfaces for long periods of time, excessive rusting (upwards of 100 to $125 \ \mu m$ or four to five mils per year) and the formation of nonprotective rust layers could prevail. Coastal zones in Louisiana as well as in many other places experience high humidity, foggy conditions, and relatively more rainfall. Bridges in these coastal zones also encounter salt in the atmosphere brought by the wind from the ocean. Though in trace quantities, the adsorption

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and accumulation of salt and pollutants on structures becomes significant over a period of time and because of this, the bridges in the industrialized coastal zones encounter more corrosive condensates.

Two major problems seen on weathering steels in bridges and in other open structures are: (1) the formation of coarse, nonadherent flake-type rust leading to greater-than-anticipated metal loss, and (2) pitting underneath the rust. This paper examines these problems to understand their modes and mechanisms of occurrence.

Field Study and Experimental

Seven bridges located in different parts of the State of Louisiana (LA) and one in the State of Texas (TX), built with grade A or grade B of ASTM A-588 weathering steel were used as representative test sites for the evaluation of corrosion problems. The locations of these bridges are shown in FIG. 1. As can be seen, six of the bridges are located in the proximity of the Gulf of Mexico, three on the western and three on the eastern sector of the state's coastline, one at the interior of Louisiana (at Leesville, or LV) and one in the far north, about 200 miles from the coastline (near the Monroe, LA-Boeuf river bridge, or BR). The one at High Island, TX (HI) is within 2 km from the Gulf and the one at Empire, LA (the Doullut canal bridge, or DC) is on the edge of a salt water lake. The youngest of the eight, the one at Luling, LA, (LU) that spans the Mississippi river, is in a semiindustrialized area. These bridges were built in the mid-seventies and the steels in these bridges have weathered in the open for nearly twelve years. The Luling bridge is about three years old.

Rusts formed on the steels in these bridges as well as from analogous bridges or structures from the States of California, Hawaii, and West Virginia were collected by hand scraping or scraping with a blade from several representative exterior (sun and rain exposed) and interior (sheltered from rain and sun) locations, brought to the laboratory, and subjected to several analytical tests.

Chloride was found in the rust by dissolving the digestible salt fractions in the rust in deionized, distilled water and using chloride-sensitive electrodes. The elemental make-up of the rust was determined by dissolving it in nitric acid (HNO₃) and using the atomic absorption technique. The average size and thickness of rust flakes and particles and sheets of rust were established. The structures of rust phases were elucidated using X-ray diffraction (XRD) and infrared absorption spectrophotometry (IRS), and the morphology and growth characteristics of rust phases in selected samples were found using scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDXA). The results obtained are discussed elsewhere [2,3], and in this paper an attempt is made to correlate the rust particle (flake) size data with the chloride content in the rust samples.

A pitting evaluation of the steel in the bridge sections was carried out in-situ at the bridge site after sand blasting the steel at selected representative locations to white metal to clean the surface and the pits from rust and corrosion products. The depths of pits were measured using a sensitive digital, linear gage (Model EG 307, Ono Sokki, Japan), by mounting it in a "Zero It" translator held on a magnet, and holding it above the locations of the pits. Depths of about ten pits were usually measured at each location, from which the maximum as well as the average pit depth were determined. More readings were taken at locations where pit depth profile analysis was desired. Both exterior and interior locations were examined, though more spots were chosen for the interior, sheltered parts of the bridges. Such interior locations were on vertical walls facing different directions, horizontal and inclined surfaces facing up and down, partially or completely closed boxed locations where water normally collects and remains, and surfaces on girders, beams, etc. These were also clustered at two strategic points, one on either side of the bridges at pier locations, in two different piers.





Results and Discussion

Flaking

The rust on the weathering steels generally occurs as flakes (grains) or particles. The exterior sun-exposed surfaces have fine powdery rust particles of an average diameter of about 0.5 mm. This is caused by repeated washing of the rust by rain, which not only removes some rust but prevents the particles from growing into coarse flakes or grains. The sun exposure may also play a role in stabilizing the thin amorphous rust layer that is found at the rust-metal interface.²

The exterior surfaces are generally devoid of any serious corrosion problems. They show no pitting or excessive metal loss. In dusty areas where dust accumulation is appreciable, the rust particles on such exterior surfaces tend to get somewhat coarse, still $\leq 1 \text{ mm}$ in size.

The rust formed at the interior, sheltered locations tends to be flaky or sheet-type. Stratification is observed in the sheet-type rusts as well as in flakes, indicating different growth kinetics depending on seasonal variations. Larger amounts of rust are likely to form during the wet rainy or winter seasons than during the dry summer months, the latter essentially curtailing the growth. Other factors, hitherto unidentified, such as phase transformations, may play dominant roles in the demarkation of various layers [2,3]. X-ray diffraction and electron microscopic analysis shows that during drying, a portion of the rust, found especially at the interface between layers, gets converted from γ -FeOOH to α -FeOOH or δ -FeOOH form underneath the top layer. The formation of an α form of rust probably leads to loss of adhesion between different layers also.

Large sheet-type rust with two or three layers has been found on the steel at the Luling bridge [2]. This is a new bridge and the sheet-type rust seems to have developed from a sedimentary rust deposit that has dried. There are not that many cracks in these sheets, which indicates that the rust may not have dried appreciably, retaining some moisture all along. Similar sedimentary-type rust sheets are formed in such areas where water pooling and retention is excessive. The presence of salt in the stagnant water accelerates rusting and leads to the formation of thick rust sheets.

Generally, the rust formation in sheets occurs in partially enclosed boxed locations at the entrance to the piers where water accumulation and retention are rather high. The rust formed in such boxed locations, not only on the steel plates but on the bolt heads as well, is thick, nonuniform, and stratified, and deep pits have been observed in the metal underneath. The stratified sheets also occur at the edges of steel plates in such boxes.

The sizes of the rust flakes formed on the steel surface at the interior, sheltered locations show good correlation to the chloride content in the rust. The sizes of flakes from several bridges are given in Table 1, in which the chloride-content of the rust samples as well as the pH of solutions extracted from them are also indicated. The sizes generally vary over a range and, hence, the maximum and average particle sizes observed are used in the analysis. These sizes are not felt to be affected by the method of rust removal. The flakes are very coarse, sharp-edged, and loosely attached to the metal in such bridges as Doullut canal (DC) and High Island (HI), which are in close proximity to the ocean or salt water lakes. The atmosphere at these locations is not only highly humid, it carries larger amounts of salt coming from the salt water.

The flakes are about 3 to 5 mm in mean diameter, when the chloride content in the rust is high—2.5 to 6.5 ppm. As the chloride content decreases, so does the flake size (Fig. 2). When the chloride content drops to below 1 ppm, the flakes are very fine, with an average diameter of about 0.5 mm. There is thus a direct correlation between the chloride content and the size of the rust flakes.

High chloride content in the condensed water in the rust would be favorable for moisture absorption and retention, which in turn would enhance the corrosion rate. In addition, the

²Raman, A. and Sharma, L., "Application of Infrared Spectroscopy in the Study of Atmospheric Rust Systems, (ÿ) Rusting of Weathering Steels Under Exterior, Bold-Exposure Conditions," to be published.

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	TABLE 1–Rust Flake Sizes an	d Chloride Conten	ts in Representative Rusts fron	m Various Bridges.	
	Rust Particle Size,	шш			Distance from
Bridge Designation	Maximum	Average	pri of Extract with Distilled Water	Cl⁻, ppm	Ocean or sait Water Lake, km
DC (eastern part)	5.0	3.0	7.5 to 8.5	2.5 to 6.5	0 (lies at the edge of a salt
HI (western part)	4.5	2.0	5.0 to 6.5	4.7	water lake; U content: 3400 ppm) ~ 1.5
			(in flakes) 7.5 to 8.5	(in flakes) 1.5 to 5	
LR (eastern part)	3.5	01	(in a sheet of rust)	(in sheet) 1 to 2	~ 10
GT (western part)	2.5	1.0		<1 to 1.5	~ 15
LU (eastern part)	1.5	1.0	:	ī	~ 10
	sheets: up to 2.5 mm thickness in 3-layered samples		8 to 8.5	0.8 to 1.6	
LV (central part) BR (northern part)	0.75 0.75	0.5 0.5	5.7 to 7.3 5.8 to 7.9	(in sheets) 0.6 to 1.2 0.5 to 1.5	~ 150 ~ 300



FIG. 2-Dependence of rust particle/flake size on chloride content in the rust.

chloride salts of the metals, such as ferrous chloride, would hydrolyze water and increase the acidity of the electrolyte in the process, which would enhance the corrosion rate of steel.

The average section thickness losses caused by rusting and corrosion occurring at different places were determined by directly measuring the thickness of the steel at several chosen locations in different bridges annually. The data collected over a two-year period indicated roughly two times the average thickness losses derived with field coupons at various sites. The data, however, are in conformity with the average thickness losses that can be derived from pit depth measurements. The obtained values are given in Table 2. Thickness losses of 50 to $125 \ \mu m$ or two to five mils per year were found for weathering steel in sheltered regions under the bridges located in the Gulf Coast area. Average losses of 1 to 2 mils per year derived from weight loss data of the field coupons conform with the values reported by McKenzie [4] for weathering steel in bridge spans in England. McKenzie has also reported data on pitting that are similar to data obtained in this work. Because of the saline atmospheric conditions, the losses determined in this work are attributed to atmospheric chloride derived from sea salt.

Pitting

Pitting is another problem on steels in coastal area bridges. It snows rarely in Louisiana and deicing salts are used only occasionally. Hence the problem is not from deicing salt usage. Steels on bridges located far away from the coastal area, such as at Leesville (LV) and the Boeuf river (BR), do not show any serious or measurable pits.

The maximum and average depths of pits from several readings taken at various locations on four of the six coastal area bridges on which measurements were made are given in Table 3. The averages of all the maximum readings and the average readings at similar locations in the different bridges given in Table 3 are included in the last two columns of the Table, from which some general conclusions are drawn and interpreted in the following:

1. Sun and rain exposed exterior surfaces generally are devoid of pitting or show very fine and very shallow pits, so closely located that it can be construed as a general form of uneven attack.

2. Maximum pit depths are seen in partially enclosed boxed locations (#5 in Table 3), where wild life in this area, such as owls, shelters and builds nests. Maximum depth readings of about 1.3 mm (52 mils) have been obtained at this location in the Doullut canal bridge. The average of all maximum values from the four bridges in the Table is 0.7 mm (28 mils) and the average of all readings in the boxed areas is about 0.42 mm (17 mils).

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	Average Section Thicks	ness Losses, mils/year ^a
Bridge Locations	Exterior Vertical Surfaces	Interior walls, Horizontal and Inclined Faces
ZONE 1	: Mild, Rural Atmospi	IERE
Boeuf river (BR)	about 1	inconclusive
Leesville (LV)	inconclusive	inconclusive
Average	about 1	
Estimate from field		
coupon data	about 0.2	about 0.5
ZONE 2: MEDIUM SEVE	re, Industrial, Near C	oastal Atmosphere
Forked Island (FI)	2 to 2.5	inconclusive
Gibbstown (GT)	2 to 3	2 to 4
Luling (LU)- (approach span)	2 to 3	2 to 3
Larose (LR)	inconclusive	2 to 3
Average	2 to 3	2 to 4
Estimate from		
field coupon data	about 1	1 to 1.5
From pitting data		2 to 4 ^b
ZONE 3: Severe, Near	Marine Atmosphere, C	LOSE TO GULF COAST
High Island (HI)	3	4 to 5
Doullut Canal (DC)	3	3 to 4
Luling (LU)-	1.5 to 2	4 to 5
Main Span		
Average	3	3 to 5
Estimate from		
field coupon data	1 to 2	1.5 to 2
From pitting data		2 to 5 ^b

TABLE 2—Average section thickness losses obtained from direct measurements at various locations in bridge spans in Louisiana and Texas.

"Multiply the values by 25 to convert to μ m/year.

^bConservative estimates from the average and maximum pit depths measured. The losses could be higher than these values since some of the metal in the pitted area is also being uniformly corroded off. Thus the maximum values could be higher by 0.02 or 0.04 mm or one or two mils in selected localized areas of attack.

Such deep pits have also been found at the open edge locations of a pier in the Luling bridge. The highest reading of 1.03 mm (41.2 mils) is equivalent to similar readings obtained in boxed locations.

The pits at these locations are also considerably wider compared to pits at other locations. They are generally round and about 6 to 12 mm (0.25 to 0.5 in.) in diameter.

Such wider and deeper pitting is caused by excessive rusting when water remains stagnant in this area or the rust stays wet for longer periods of time. The characteristics (composition, pH, etc.) of the rust formed under the debris were not studied and, as such, the effects of the birds' nesting cannot be assessed. Since deep pits have also been found at Luling and in Hawaii in areas where birds have not taken shelter, the bird excretions may not be a factor. However, the nests and debris would block the flow of water and thereby contribute to the collection of stagnant water and thus increase corrosion. Although there are drainage holes, they get clogged also. Periodic cleaning and removal of the debris and rust collecting at this location should minimize the severity of the attack considerably. TABLE 3-Maximum and average pit depths at selected toration. 1 representative bridges (data in parenthesis refer to analogous locations on another pier, on the opposite side of the bridge).

						Wotow	a Sactor			
		Easter	rn Sector			wester	n sector			
	Luling	(LU)	Doullut Ca	unal (DC)	High Isla	(IH) pu	Gibbstow	vn (GT)	Averages A	Il Bridges
Location in Bridge	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average	Maximum	Average
1) Vertical face on the	9.7	5.8	12.0	7.7	7.4	4.5	0.6	5.6	8.8	5.6
side wall (inner,	(nearly e	quivalent	(0.0)	(6.1)	(7.3)	(4.3)	(7.3)	(5.4)		
sheltered side) 2) Vertical face on inner	24" 24"	ace) 9.1"	œ	6.2	7.0	6.2	8.7	5.7	8.8	6.2
web plate			5	•	(6.7)	(2.1)	(13.5)	(7.7)		
3) Horizontal beam on	:	:	10.5	7.2	13.3	10.5	10.5	7.3	10.2	7.5
pier, facing up			(12.9)	(10.4)	(6.8)	(4.7)	(2)	(5.1)		
4) Horizontal beam on	19.5	8.8	10.4	10.1	18.3	16.3	8.0	5.9	13.2	9.3
pier, facing down	(14.8)	(6.5)	(14.0)	(10.3)	(9.6)	(6.2)	(11.0)	(2.3)		
5) Boxed location over	41.2	21.8	52.45	11.6	::	:	32	22.2	28.7	16.8
gusset plate, facing up	(equivalen	t location)	20.2	(10.6)			(30)	(17.8)		
6) Wardenstaf and a			(0.02)	1 4	10.2	12	11 7	X X	14 8	10.4
of morizonital surface,	:	:	C.C7	10.4	10.01) ج 2	1			
facing up, on gusset			(12)	(10.3)	(17.3)	(8.7)	(0.0)	(1.c)		
plate, outside of box			ç				15.7	V C1	1.2.1	5 0
/) Horizontal surface,	;;	:	13	10.3	:	:	1.01	12.4	1.21	2.
facing down, on gusset							(<./)	(6.0)		
plate, outside of oox 8) Edan flamme of the			131761	10.2	0 2	4 S	5 S	43	80	7.0
entrance to the pier,	•	:	(16)	(11)	с.,	2	(9)	(4.9)	2	
facing down										
9) Inclined beam, top	7(7.9)	6(5.2)	7(7)	5.5(5.8)	15.7	11.6	16.5(11)	10.3(9.6)	10.3	7.7
surface				f 0,0		C V F	10/61	11 6(4 6)	12.8	с С
IU/ Inclued beam,	•	•	(71)07	10.11	12.7	10.2	10/01	(0.F)0.11	0.01	2
00(10m Surface									103	7.6
									13	9.2
(1) and (2)									8.8	5.9

RAMAN ON ATMOSPHERIC CORROSION OF WEATHERING STEELS

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^bFew such high readings were obtained; they do not include also perhaps some general thickness loss. ^cMultiply mil by 25 to get values in μ m.

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3. Not only the horizontal surfaces in boxed areas, but similar upward-facing surfaces outside boxed locations (#6 in Table 3) do experience greater than average pitting as well. This is again caused by the rust and debris collecting at such points, preventing water from draining.

4. Pits, somewhat less severe, but about half the size of the pits seen in the boxed locations, are seen on the bottom surfaces of horizontal and inclined beams (#4, 7, 10 in Table 3). The average of the maximum readings on such surfaces from various bridges is about 0.32 mm (13 mils) and the average of all the readings is about 0.23 mm (nine mils). In comparison, the pits on similar beams, on surfaces facing upward (#3, 9 in Table 3), are slightly less deep. The average value of the maximum readings is about 0.25 mm (ten mils) and the average pit depth from all readings is about 0.19 mm (7.6 mils). The readings on the top surfaces were consistently smaller than the readings on the bottom surfaces.

The reasons for the somewhat larger pits on the bottom surfaces of beams are not readily discernible. Even if one would argue that these values are about similar for both the top and bottom surfaces, the very fact that the surfaces facing down show somewhat wider and deeper pits is important, for it possibly points to a mechanism of pitting on steels not dependent or controlled by gravitational forces. Given similar circumstances, one could expect more rusting and deeper pitting on the top (skyward) surface than the bottom (groundward) surface because of more water dripping off from the bottom face. It is possible that in this process or otherwise some rust falls off from the bottom face, thus exposing fresh metal. This could explain the observations.

5. The bottom surfaces of girder beams at the edges on both sides of the bridges (#8 in Table 3) seem to experience less severe pitting than the bottom faces of the inner beams. This could be from somewhat better drying caused by more aeration and heating of the exterior plates by solar radiation.

6. The vertical faces of the beams and side plates (#1, 2 in Table 3) experience perhaps the least amount of pitting. The average of maximum pit depth is about 0.22 mm (nine mils) and the average of all readings is about 0.15 mm (six mils). These low values can be explained by considering that the vertical faces hold less of the water that collects and drains down continuously.

The above discussions pertain to maximum as well as average pit depth values at different locations. The bridges are about twelve years old and the maximum pit depths of 1 to 1.2 mm (40 to 50 mils) obtained after sand blast cleaning, which itself would remove some thickness of the metal, would give rise to about 0.1 to 0.12 mm (four to five mils) in average thickness loss per year. Assuming an average loss of metal from uniform corrosion of about 0.02 to 0.04 mm (1 to 2 mil) per year (a conservative value; see the comment under Table 2), the maximum pitting rate could be about 0.12 to 0.16 mm (five to seven mils) per year in localized areas. It should be realized that pitting is a statistical phenomenon. That is, pits of different pit depths would be seen at all locations, though, pits of about the average size would prevail widely. This implies that shallower as well as deeper pits, though smaller in number, would be found at each location. This prompts the need for pit depth profile studies.

The pit depth profiles for four different locations on the Luling bridge are shown in Fig. 3. All of them show bell-shaped plots. Figure 3a shows pit depth variations at a spot corresponding to the boxed locations, where water pooling was high. Sheet-type rust was found in this area. There are more pits in the 0.35 to 0.5 mm (15 to 20 mils) range than in other ranges, giving a peak at around 0.45 mm (18 mils) in the bell-shaped profile.

Figure 3b corresponds to the nearly vertical face of a trapezoidal box corresponding to location #1 in Table 3. This figure shows that there are more pits in the 0.1 to 0.2 mm (four to eight mils) depth range than in others. Likewise, Fig. 3c and 3d, which represent pit depth profiles corresponding to location 2 in Table 3 (vertical face at the interior) and location 4 in Table 3 (horizontal surface on beam, facing down), show that more pits occur in certain depth ranges than in others. The peak occurs at a pit depth value close to the average of all values.



FIG. 3—Pit depth profiles for selected interior (sheltered) locations in the Luling Bridge-Main Span (A588-grade A, Kawasaki Steel).

The number of pits ranged from 1.5 to 3 per cm² (10 to 20 per in.²) in most locations, but was much less, about 0.8 per cm² (5 per in.²), in the boxed areas. The pit density was much larger wherever fine pits were seen.

Pitting Mechanism

In deducing the mechanism for pitting on the weathering steels, the following have to be taken into account:

1. In Louisiana and Texas, pitting occurs only in coastal area bridges, which rust a lot and form coarse flakes. Bridges located inland that form fine powdery rust in the sheltered areas do not show any serious pitting. Likewise, the exterior sun-exposed surfaces do not show pits.

2. Wider and deeper pits are noticed under multilayered flakes or sheets of rust in regions where water collects and stays for a long period of time or the rust remains wet, as for example in partially boxed locations or under the rust and bird debris.

3. The larger the size of the rust flakes, wider and deeper are the pits.

4. Pitting occurs to a nearly equal extent in grade A and grade B varieties of ASTM A-588 steel. Grade B is in use in the High Island bridge, whereas grade A is found in others given in Table 3.

5. Pitting occurs to a nearly similar extent on different varieties, of grade A steel having slightly different compositions, containing normal (up to 0.05%) or very low concentrations (<0.005%) of sulfur. Thus, the grade A variety in use at the Luling bridge that contains very low amounts of sulfur pits to nearly similar extent as the grade A variety at other bridges. Thus,

the extent of pitting does not seem to depend on the amount of sulfur or the sulfide inclusions present in the steel.

6. The pH of the solution extracted from the rust using distilled water is generally about seven to nine, that is it lies in the slightly alkaline range. However, some of the rusts from the grade B varieties under similar conditions have given lower pH values in the range of five to seven. These are for rusts in the interior, sheltered locations of bridges where rain is not a factor affecting pH. Pitting has been found underneath all these rusts. Thus, pitting in the sheltered locations seems to occur at all pH ranges. In this context, it can be noted that no pitting has been observed on grade B varieties in the northern bridges in the State of Louisiana, even though the pH of the extract from some of the rusts collected from these bridges gave values in the slightly acidic range.

All the above mentioned facts can be reconciled by employing the well known "Differential Aeration Cell Mechanism" developed by Evans. The principle of how these cells cause pitting in steels is illustrated in Fig. 4. As early as 1924, U. R. Evans [5] suggested the principle of such cells to explain the pitting attack at the central regions of a salt solution droplet held on the steel surface. Evans states that "differential aeration is a factor of rather special significance" for steels [6].

The differential aeration principle calls for the depletion and eventual lack of oxygen in the central regions of such droplets, whereas the peripheral regions get a continuous supply of oxygen. The oxygen-starved central regions become anodic and corrosion progresses by the introduction of Fe^{2+} -ions into the anolyte. The increase in positive charge concentration in the anodic regions leads to the attraction and diffusion of anions (chloride ion diffuses faster than the oxide ion) toward the central anodic regions of such droplets, accumulation of which leads to the formation of ferrous salts (ferrous chloride) in the anolyte. Supersaturation of the anolyte could lead to precipitation and deposition of a porous salt layer on the active anodic site. Such salt deposits have indeed been observed [7,8].

The ferrous chloride as well as other such salts formed in the central regions of droplets hydrolyze the water, leading to the accumulation of H^+ ions and a lowering of the pH to acidic levels. The liquid in the pits of iron has been shown to contain 4.6 *M* FeCl₂ in chloride solutions, with the pH dropping to about 3.8 [9].

Early works discussed by Evans [6] and Wranglen [10] as well as the works of Szklarska-Smialowska [11], Wranglen [10], and Gainer and Wallwork [12] indicate that pitting in steels starts at the sulfide inclusions.



STRATIFIED RUST



DIFFERENTIAL AERATION CELLS

(A) EVANS SALT SOLUTION DROPLET MODEL (B) PROPOSED MODEL FOR PITTING UNDER A RUST MOUND OR FLAKE

(C = Cathodic, A = Anodic, F = Site of First Attack)

FIG. 4—Mechanism for pitting in steels and formation of stratified rust mound.

Various reactions that take place at the cathodic and anodic areas in and around the pit, nucleated and grown by sulfide inclusions, are given by Wranglen [10]. Essentially, these include the formation of H_2S , HS^- , and S^{2-} ions in the anolyte, which enhances the corrosion rate. At the resultant pH of about 3.5, the normal sulfide inclusions in steels would dissolve, leading to the formation of these species.

The pit has a tendency to grow laterally and expand because of the "well known power of alkali (that diffuses to the peripheral cathodic sites) to creep over dry metal" [6]. The rust forming reactions occur in the regions midway between the cathodic and anodic areas, leading to the formation of ferrosoferric oxide (Fe₃O₄) or FeOOH [6]. The formation of rust prevents mixing of anolyte and catholyte, leading to the prevalence of occluded cells [9].

Pourbaix [9] has shown that when the pH is about the same in both the aerated peripheral as well as the nonaerated central regions of a differential aeration cell, the cell will operate freely if the pH is maintained in the eight to ten range [13]. This is because passivation of steel occurs readily in this pH range on the cathodic sites. The potential of the cathodic regions increases, whereas the potential at the active interior regions would remain more negative and anodic. The large potential gradients are explained by Pickering and Frankenthal [14] as caused by the IR drop in the anolyte from H_2 gas bubbles evolved within the pit.

A similar mechanism can be invoked to account for pitting on weathering steels. The sulfide inclusions could help in nucleating the pits, but they are not absolutely necessary. The steel, as it rusts, could be expected to form more rust in some regions than in others because of condensation and the uneven accumulation of water droplets. Wherever more water remains, more rusting occurs. Such areas in sedimented rust layers or in rust mounds would act like salt solution droplets on the steel surface. There will be more air and oxygen supply to the peripheral cathodic regions and correspondingly less oxygen supply to the central regions of such rust mounds or spots. If chloride or sulfate salts are present, one could expect a concentration of these salts at the central regions creating similar situations as in Evans' model. The differential aeration cell mechanism would then function, causing more dredging of the metal at the central regions of the rust mound, which eventually becomes a stratified flake. Such rust mounds as those shown in Fig. 4b have actually been observed in Hawaii. The pit does not grow deep, but spreads laterally because of reasons already cited.

For this proposed model to work, the flake or the mound must be semiadhered to the steel surface. This seems to occur readily. Depending on seasonal variations, stratification occurs and, theoretically, a spiral-shaped, hemispherical pit, as illustrated by Shreir [15] should result. However, most of the pits found on weathering steels do not have such shapes, probably from the uneven distribution of condensed water and/or diffusion of cations toward the peripheral zones.

Conclusions

Excessive rusting, formation of coarse flakes that adhere loosely to the steel, and pitting are some of the common problems encountered in weathering steels in bridges exposed to humid, salt-laden atmospheres in the coastal zones of Louisiana and Texas.

The flake size is proportional to the chloride-content in the rust. The higher the chloridecontent, the coarser, thicker, and sharper the flakes. Thus, coastal area bridges develop coarse flakes that peel off easily.

Section thickness loss is maximum at some localized, interior sheltered locations, as much as 0.04 to 0.10 mm (two to five mils) per year in some of these bridge spans, caused mainly by chloride accumulation.

The bridges far away from the coastal region as well as the exterior surfaces of all bridges in Louisiana and Texas develop fine, powdery rust and do not show any serious corrosion problem. In places where salts are used extensively for deicing purposes, the situation could be different.

Pits are generally found in the sheltered areas in the coastal zone bridges. The pitting appears
to be related to flake size, rusting rate, section thickness loss, and the chloride content of the rust. Deep pits occur in regions where the chloride content is high and the thickness loss is maximum, and vice-versa. Most of the pits are about 0.25 mm (10 mils) deep in the interior locations of the bridges after about twelve years' exposure. The horizontal as well as the inclined surfaces at the interior, sheltered locations, facing down, seem to have somewhat deeper pits than the analogous surfaces facing upward. Vertical surfaces experience the least severe pitting. Partially enclosed boxed locations and regions where water accumulates and stagnates a lot develop wider and deeper pits. Pit depths of as much as 1.3 mm (52 mils) have been recorded here. This is probably caused by excessive rusting (about 0.1 to 1.02 mm or 4 to 5 mils per year loss as opposed to about 0.02 mm (1 mil) per year average normal loss) in the presence of stagnant water pools or highly wet rusting conditions. Chloride and salt accumulation is also higher in these areas. Serious metal loss (more than 125 μ m per year (five mils per year)) occurs here (see comment under Table 2).

The mechanism of pitting on weathering steels in bridges is dependent on the formation of differential aeration and occluded cells. Sulfide inclusions may activate the pitting tendency, but the mechanism of pitting on weathering steels does not seem to require such sulfides or other inclusions to nucleate the pits.

Uneven wetting on the surface and retention of water in some areas more than in others would cause more rust to form in such regions, which would activate the formation of differential aeration cells. More rusting occurring underneath such regions and seasonal variations of the rusting kinetic lead to the stratification of the rust mound and to lateral spreading or widening of the pitted areas. As such, sharp and deep pits do not form, but wider and less deep pits occur as on regular structural steels, such as ASTM A 36.

Increased salt (chloride) content in the atmosphere and, hence, in the rust enhances the rusting and pitting rate. Hence, the deepest and widest pits have been observed in chloride-laden areas.

If left unattended and uncorrected, such severely pitted and rusted areas would weaken the structure considerably. Boxed locations in bridges need the maximum attention.

Acknowledgments

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DISCUSSION

H. E. Townsend¹ (discussion question)—Steels at the strength level (50,000 PSI Minimum yield strength) of weathering grades (ASTM A 242 and A 588) are generally felt to be resistant to stress corrosion cracking, except in the presence of certain specific environments such as hydroxide and nitrate. Why then do you state that you expect to find stress corrosion cracking in structures made of these materials and exposed to the atmosphere?

A. Raman (author's closure)—There are many unknowns and practically no experimental work has been undertaken to study the characteristics of weathering steels under conditions that would induce stress corrosion cracking (scc). I feel that scc would be possible in some of these varieties, especially at the highly stressed areas, because of the following reasons:

1) Some of these varieties have fairly low fracture toughness values, just enough to meet the specifications, say 15 to 20 ft-lbs at 0 deg.C.

- 2) They have quite a bit of sulfide inclusions and some of them have pinhole porosities.
- 3) The strength level is high enough to enable cracking in the scc mode.

4) As is known, during the scc the crack tip potential varies back and forth due to passivation and depassivation or film rupture, etc. processes, and such variations are found to be possible in the case of weathering steels that produce massive corrosion products. The rest potential has been found by us to vary by as much as 200 mV in chloride solutions toward the more negative side. (Unpublished results). Such variations occur during passivation and passive film rupture, in our case the thick film rupture.

5) Hydrogen evolution reaction is the dominant cathodic reaction in chloride media. (Unpublished results). The hydrogen produced could aid the crack growth. Thus, if not pure scc, hydrogen assisted scc would be possible.

6) In atmospheric exposures under neutral conditions of electrolyte fairly large amounts of hydroxides are produced and the pH goes up (unpublished results). This could aid scc.

It is also not wise to treat all exposure conditions equally and exclude the possibility of scc totally.

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Effects of Weathering of Chromate Passivation Films on Aluminum-Zinc Alloy Coated Sheet Steel

REFERENCE: Cleary, H. J., "Effects of Weathering of Chromate Passivation Films on Aluminum-Zinc Alloy Coated Sheet Steel," *Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 30-34.

ABSTRACT: This paper presents a study of the effects of surface chromate passivation treatments on the corrosion rate and appearance of 55% Al-Zn coatings on sheet steel after weathering in an industrial atmosphere for a period of six years. Weight loss measurements were employed to determine corrosion rates, and surface appearance was evaluated by photoelectric reflection meter measurements and visual observations. It was found that increasing amounts of chromium (Iridite 9L6) applied to the surface of 55% Al-Zn coated sheet steel markedly decrease both the corrosion rate of the coating and the rate at which the surface gradually darkens in appearance and loses reflectivity caused by weathering. The bright reflective surfaces observed on six-year-old specimens with 14 mg/m² chromium on the surface indicate that this level is a suitable minimum for preventing nonuniform weathering appearance problems and for optimizing the corrosion resistance. The applied surface chromium should not exceed about 31 mg/m² chromium because of yellow surface discoloration at these higher levels.

KEY WORDS: chromate coatings, weathering, zinc-aluminum alloys, coatings, atmospheric corrosion, corrosion tests

Al-Zn coated sheet steel is currently in widespread use as roofing and siding in metal buildings [1]. The coating consists of 55% aluminum, 1.6% silicon, and balance zinc (by weight) and is applied to steel sheet by the continuous hot-dip process. Developed by Bethlehem Steel Corporation and marketed in the United States under the trademark Galvalume, the material reportedly offers over two times greater life in atmospheric environments than galvanized steels having equivalent thickness zinc coatings [2].

Just before final coiling on the production line, a clear protective chromate conversion file is applied to the coated sheet steel surface using Iridite 9L6 (Trademark of the Richardson Company, Des Plaines, IL). The main purpose of this treatment is to provide protection against wetstorage staining corrosion that can occur on coiled or stacked sheets in humid environments. The total amount of chromium deposited on the sheet surface can be varied by adjusting chromate solution composition, temperature, and immersion time.

Previous studies have been devoted to defining the amounts of deposited chromium required for adequate protection against storage staining [3] and X-ray photoelectron spectroscopy (XPS) analysis of typical chromate passivation films [4]. This report deals with studies of the effect of chromate treatments on the corrosion rate and appearance of the Al-Zn coating during weathering in the atmosphere.

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Test Results

Inspections of a number of buildings were made in response to field reports that color variations were occurring on roofing made with Al-Zn coated sheet steel. The nature of this nonuniform weathering appearance is illustrated by Fig. 1, which shows an area on a roof after atmospheric exposure for about seven months. The initially bright and shiny roofing sheets have darkened at different rates during weathering. This phenomenon has been observed on nearly flat as well as sloped roofs. Sheet specimens taken from the area shown in Fig. 1 were examined in the laboratory. The light-colored area (Panel 3B) was found by wet chemical analysis to contain 8 mg/m² of total surface chromium whereas the dark-colored area (Panel 3A) contained only about 2 mg/m². In order to ascertain the initial levels of chromium before atmospheric exposure, the unexposed (underside) surfaces of the two panels were analyzed and were found to contain the same level of chromium as the exposed surface in each case. Thus, it is reasonable to assume that no significant loss of chromium occured on the exposed side. No correlation was evident between the degree of discoloration and bulk coating composition, coating microstructure, or coating thickness.

A more extensive study was then performed on a series of commercial Al-Zn coated sheets produced with various levels of applied surface chromate. Specimens, 10.2 by 15.2 cm, were exposed to the atmosphere at Bethlehem, PA, for about six years. Photographs of typical specimens for each of four different surface treatments are shown in Fig. 2. Note that the relative brightness of the surfaces is related to the amount of chromium deposited by the passivation treatment, with the brighter panels containing higher levels of chromium.

These specimens were examined further in the laboratory by means of a Photovolt Corporation Model 610 Photoelectric Reflection Meter in order to quantitatively characterize their appearance. Three diffuse reflectivity readings were obtained on each of eight replicate specimens of each material. The meter was calibrated using a Gloss Standard 60-213-35 (Gardner Laboratory, Inc.). The average diffuse reflectivity (plus or minus one standard deviation) is plotted in Fig. 3 versus the amount of deposited chromium. In accordance with the visual appearance, brighter, more reflective specimens contained higher initial surface chromium levels, and darker, less-reflective surfaces had less chromium. The change in slope of the curve at less than $9-mg/m^2$ chromium may be related to the required minimum of 6 mg/m² chromium found to prevent wet-storage stain in laboratory wet-pack tests [3]. This level of 6 mg/m² also corre-



8.0mg Cr/m²

1.7mg Cr/m²

FIG. 1—Color variations on Al-Zn coated steel roof in Northeastern United States about seven months after exposure.

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FIG. 2—Photographs of typical 10.2 by 15.2-cm Al-Zn coated specimens exposed for six years at Bethlehem, PA.

sponds to the point where the passivation film begins to incorporate water-soluble (hexavalent) chromium compounds in addition to the water-insoluble (trivalent) chromium compounds deposited at lower total applied chromium levels. In other words, at low levels of applied chromium the element is present in the film primarily as trivalent oxide whereas, as the total applied chromium increases above 6 mg/m², a new surface layer forms which essentially consists of a hexavalent chromium compound [4]. It has been suggested that the availability of this water-soluble hexavalent chromium is needed to attain higher levels of protection in the wet pack corrosion test [3].

Corrosion products were removed from duplicate (10.2 by 15.2-cm) specimens of each material using 20% chromic acid at 80°C for 1 min, and corrosion weight losses were determined. The Fig. 4 plot of the weight loss (average \pm standard deviation) versus initial surface chromium reveals the beneficial effect of higher chromium levels on lowering the corrosion rate. The weight loss of the 19 mg/m² chromium specimen is 38% lower than that for the 1 mg/m² chromium specimen. As in Fig. 3, there is an apparent change in slope of the curve at less than 9 mg/m² chromium, which again may be related to the incorporation of water soluble chromium as discussed above.



FIG. 3-Discoloration of six-year exposure specimens.



FIG. 4-Weight loss of six-year exposure specimens.

Conclusions

Based on the bright, reflective surfaces observed on the specimens with a level of 14-mg/m^2 chromium (Iridite 9L6) in Fig. 2, we believe that this level is a suitable minimum for outdoor applications where surface appearance is an important consideration. The surface chromium should not exceed 31-mg/m^2 chromium because of yellow surface discoloration at these higher levels.

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DISCUSSION

V. S. Agansula¹ (written discussion)—It was suggested that the top surface contain Cr^{+6} , which is soluble chromate and helps in protecting the substrate. How can you assume that it was a hexavalent chromate and not a trivalent? In most chromate coversion coatings Cr^{+6} treatment produces Cr^{+3} as Cr_2O_3 such as in alodine treatment. We have found no evidence of Cr^{+6} at all ever under XPS analysis.

H. J. Cleary (author's closure)—The reviewer is referred to Refs 3 and 4 of the paper. Both water-soluble and water-insoluble chromium compounds have been found to be present in chromate passivation films. The water-soluble (hexavalent chromium) unreacted portion of the film is not observed until the total chromium in the film exceeds 6 mg/m²[3]. The reviewer may not have employed the processing conditions required to produce such films. Moreover, XPS measurements have demonstrated the presence of hexavalent chromium at the outer surface of the film [4].

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The Corrosion of Stainless Steels in the Atmosphere

REFERENCE: Kearns, J. R., Johnson, M. J., and Pavlik, P. J., "The Corrosion of Stainless Steels in the Atmosphere," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Ed., American Society for Testing and Materials, Philadelphia, 1988, pp. 35-51.

ABSTRACT: A total of 38 types of stainless steel have been exposed for 1 to 15 years at a coastal site and 32 years in a semirural atmosphere. The resistance of stainless steels to degradation in the atmosphere was directly related to alloy chromium and molybdenum contents. Only American Iron and Steel Institute (AISI) Type 410 showed any signs of corrosion in the semirural environment. Significant corrosion product tarnishing occurred on all nonmolybdenum-bearing stainless grades after only one year of exposure in the marine atmosphere. Stainless grades that had been sensitized by an autogenous welding operation were susceptible to preferential corrosion at weld and heat-affected zone surfaces when exposed at the 250-m lot on Kure Beach, NC. Galvanic attack and corrosion product staining was observed for certain dissimilar metal couples between AISI Type 304 and other commercially pure metals, nickel-base and copper-base alloys. A photometric technique was used to quantitatively describe subtle changes in the appearance of three stainless steel surface finishes during exposure in a semirural atmosphere.

KEY WORDS: atmospheric corrosion tests, stainless steels, nonferrous metals, galvanic corrosion, tarnishing, sensitization, colorimetric measurements

Alloys of iron that contain at least 10.5 wt% chromium appear to remain "stainless" in unpolluted rural atmospheres. Increasing the chromium content of a steel decreases the amount of weight loss caused by corrosion [1-5], which is related primarily to a change in the mode of attack from uniform corrosion over an entire specimen surface to more localized pitting, as noted in Fig. 1. The corrosion products from very shallow pits can stain the surface of a ferrous alloy containing more than 12 wt% chromium in polluted and marine atmospheres. Specific combinations of other elements (for example, nickel, molybdenum, copper, silicon, and phosphorus) can significantly alter the resistance of iron-chromium alloys to all forms of corrosion (which has led to the development of over 170 different grades of stainless steel). Molybdenum enhances the resistance of stainless steel to localized attack in atmospheres containing chlorides (Fig. 2) [6-8]. Small quantities of nickel (less than 5 wt%) reduce the corrosion rates for Fe-Ni steels [9] and inhibit the propagation of pits in steels containing chromium and molybdenum. The weight loss for stainless steels exposed to aggressive atmospheres does not appear to be significantly influenced by alloy nickel content (Fig. 3) [10-13].

Moisture and particulate matter enhance the corrosive effects of gaseous pollutants, such as hydrogen sulfide and sulfur dioxide, particularly in the form of deposits on metal surfaces exposed in urban and industrial locations [14]. Such deposits can (1) isolate regions on a metal surface to create localized anodic sites and (2) concentrate corrosive species, such as chlorides

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FIG. 1—Relationship between specimen weight loss and alloy chromium content for steels exposed for four years in cited atmospheres. The mode of corrosion also changed with alloy chromium content [3].



FIG. 2—Relationship between specimen weight loss and alloy molybdenum content for cited austenitic and ferritic stainless alloys exposed for five years in an industrial/urban atmosphere [7].

or sulfuric acid, under cyclic conditions of wetting and evaporation. For example, AISI Type 430, 304, and 316 stainless steel have been observed to pit because of the combined effects of the sodium chloride and sulfur compounds present in surface deposits [15]. Aggressive chloride solutions can also form under deposits that have been intermittently wetted by sea spray. Organic acids, such as acetic and formic acid, have also been observed in atmospheric precipitation [16], but in concentrations that were too low to corrode stainless steels.



FIG. 3—Relationship between specimen weight loss and alloy chromium for cited nickel contents. Specimens were exposed for 15 years in an urban atmosphere [12].

The galvanic interaction of certain metals with distinctly different corrosion characteristics, such as Type 304 stainless and magnesium, can lead to accelerated corrosion in regions of contact. In addition, the bright or lustrous finish of a stainless steel can be marred by the corrosion products of certain nonferrous metals. The occurrence of galvanic corrosion and corrosion product tarnishing at joints between dissimilar metals has been evaluated in the present study by exposing, for over three decades, panels of American Iron and Steel Institute (AISI) Type 304 that had been riveted to a variety of commercially pure metals, nickel-base and copper-base alloys.

A bright or lustrous stainless steel surface finish can be preserved with a minimum of maintenance in architectural and automotive applications. However, changes in the appearance of stainless steels—more subtle than pitting or corrosion product tarnishing—do occur in terms of metallic color and gloss. The color of a stainless steel not only varies with the atmospheric conditions, but also depends on alloy composition, heat treatment, and surface finish. A photometric technique has been used in the present study to quantitatively describe changes in the appearance of stainless steels with various surface finishes during exposure to the atmosphere.

Experimental Procedure

Materials

Thirty-eight different types of stainless steel representing thirteen compositional classifications were tested. Chemical compositions and surface finishes for the said classes of stainless steel are given in Table 1. Specimens were cut from commercially produced sheet and strip that was typically 0.13 cm thick.

Six commercially pure metals, one copper-base alloy and one nickel-base alloy (Table 2), were exposed to characterize a test site located in Brackenridge, PA, relative to sites that had been used in previous studies sponsored by ASTM. In addition, a nickel-base alloy (INCONEL* [Trademark of International Nickel Company] alloy 600) panel, 3 panels of a weathering steel (USS COR-TEN* [Trademark of U.S. Steel Corp.] A steel), and 15 carbon steel (AISI 1006)

AISI Tune (Co	mposition,	wt%	
Tradename	Finish ⁴	C	Mn	Cr	Ni	Мо	Other
1. "Straight-o	hromium"	ferritic stair	nless				
405	2D	0.039	0.37	13.27	0.16	0.02	AI = 0.18
409 ⁶	2D	0.042	0.36	11.37	0.17	0.09	Ti = 0.46
430 ^c	CRAD	0.080	0.46	17.40	0.30	0.09	
2. "Straight-o	chromium''	martensitic	stainless				
410	2D	0.072	0.32	12.60	0.15	0.01	
3. High-chron	nium AISI ·	400 series st	ainless	_			
439	CRAD	0.042	0.34	18.35	0.27	0.14	Ti = 0.66
439L°	CRAD	0.018	0.35	18.31	0.19	0.08	Ti = 0.34
4410	2D	0.016	0.30	17.82	0.20	0.08	Nb = 0.71, Ti = 0.20
442	2D	0.080	0.44	21.85	0.30	0.02	N = 0.06
446	CRAD	0.104	0.76	24.60	0.22	0.02	N = 0.14
4. Molybdenu	im-bearing	AIS1 400 se	ries stainle	SS			
4340.0	CRAD	0.039	0.51	16.55	0.54	0.89	
444	CRAD	0.020	0.43	18.92	0.07	2.04	Nb = 0.39, Ti = 0.17
5. High-chron	nium, moly	bdenum-bea	aring ferrit	ic stainless			T 0.00 M 0.010
Alloy 26-15 ^e	CRAD	0.030	0.30	26.00	0.14	0.97	$T_i = 0.38, N = 0.019$
E-BRITE®	CRAD	0.002	< 0.10	25.9	0.13	1.00	$T_1 < 0.05, N_D = 0.10$
AL 29-4 ^{0.4}	CRAD	0.005	0.02	29.40	0.11	3.95	N = 0.014
AL 29-4C ⁶⁶	BA	0.016	0.29	28.32	0.40	3.68	11 = 0.68
AL 29-4-29	CRAD	0.006	0.05	29.60	2.20	3.90	N = 0.011
6. AISI 200 s	eries stainle	SS					
201	20	0.090	5.55	17.60	4.47	0.08	N = 0.12
201L ^ø	CRAD	0.029	6.25	16.28	4.39	0.16	N = 0.17, Cu = 0.46
202	CRAD	0.084	10.30	17.57	4.10	0.06	N = 0.11
205	CRAD	0.104	16.20	17.28	1.92	0.02	N = 0.32
/. Molybdeni	im-bearing	AISI 200 se	ries stainle	ss	6.00	• • •	
210	CRAD	0.054	8.42	19.94	6.89	2.61	N = 0.33
o. Austenitic	AISI 300 se	ries stainles	S 1 10	17.50	7.05	0.15	
301	20	0.10	1.19	17.50	7.05	0.15	6 0 22
303	28	0.06	1.22	18.29	9.48	0.34	S = 0.32
304		0.063	0.56	18.60	8.90	0.08	
304L 200	CRAD	0.022	0.94	10.00	8.72	0.22	
309		0.100	1.41	22.45	13.95	0.28	
0 Molubdom	2D	0.000	1.40	24.25	19.70	0.15	
316	2D	AISI 300 Se	1 57	35 1759	12.60	2 12	
316I b	20	0.030	1.37	17.50	13.09	2.12	
3171 0	CRAD	0.022	1.75	18 38	13 30	2.14	
10 "Stabilized	N A ISI 300	series stain	1.00	10.50	15.50	5.51	
371	CRAD		1 67	17 25	10.70	0.26	$T_{i} = 0.60 C_{i} = 0.31$
347	CRAD	0.000	1.02	18.02	9 70	0.20	$N_{\rm h} = 0.66$ $T_{\rm h} = 0.21$
11 Martensiti		eries stainle	1.57	10.02	9.70	0.55	100 = 0.00, 10 = 0.21
AIMAR 367	CRAD		0 10	14 34	6 67	0 13	Ti - 0 78
AM 363	CRAD	0.030	0.15	11 97	4 26	0.09	$T_i = 0.38$
12 High-nicke	el molyhder	um-hearing	austenitic	stainless	4.20	0.07	11 0.50
AL 904L b.d	2B	0.020	1.89	20 15	24.38	4.44	Cu = 1.48
AL-6X ^d	CRAD	0.038	1.73	20.41	23.61	6.50	11.00
AL-6XN®	BA	0.020	1.63	20.26	24.73	6.30	N = 0.19, $Cu = 0.18$
13. Precipitati	on Hardenii	ng stainless					
A 286 ^b	CRAD	0.043	1.26	14.99	24.74	1.29	Ti = 2.15, V = 0.26

TABLE 1-Partial chemical compositions for stainless steels exposed at the Brackenridge and Kure Beach test sites.

^eFinishes: CRAD—cold-rolled, annealed and descaled, 2D—CRAD and planished on dull rolls, 2B—CRAD and planished on smooth, polished rolls,

BA-(1A1) brite annealed in a reducing furnace atmosphere, and Star Brite[®] (Trademark of Allegheny Ludlum Corporation)—brite annealed, electropickled and planished on belt-ground rolls. ^bAlloy was only exposed at the Kure Beach site. ^cSamples of this grade with 2B, BA and Star Brite finishes were exposed at the Brackenridge site for one

year.

^{**0**,d}Trademark of Allegheny Ludlum Corporation.

M AS	aterials as Specified by TM B-3 Sub. VII, 1955		Corrosion Rate at Given Te	, μm/year, est Site	
Code	Description	State College	Brackenridge	New York	Altoona
A	commercial copper (99.9+)	0.434	0.622	1.382	1.387
G	commercial aluminum (99+ Al)	0.076	0.549	0.734	•••
М	brass (70Cu-30Zn)	0.447	0.712	2.403	3.048
S	nickel-copper alloy (65Ni-32Cu-2Fe-1Mn)	0.170	0.742	1.585	1.920
Т	nickel (99+ Ni)	0.216	0.514	3,658	5.639
U	commercial lead (99+ Pb)	0.318	0.263	0.383	
EE	commercial tin (99.85+ Sn)	•••	0.341	1.308	1.674
нн	commercial zinc (99.9+ Zn)	0.995	1.143	5.690	6.833

TABLE 2-Qualification of Brackenridge test site relative to established ASTM sites.^a

^oData for State College (Rural), New York (Urban), and Altoona (Industrial) per H. P. Copson [18].

panels were interspersed with the said materials on four ground-level corrosion racks at the Brackenridge, PA, site.

Test Conditions and Procedures

Brackenridge, PA, Site—Atmospheric exposure racks were constructed in 1953 on the property of the Allegheny Ludlum Corporation Technical Center, which is about 33-km north of Pittsburgh, PA. The Brackenridge Works of the Allegheny Ludlum Corporation are located to the southeast and below the test site in the Allegheny River valley. The prevailing winds move over this region from the southwest. Test panels were boldly exposed facing in a southwesterly direction at a 90° angle to the ground (Fig. 4). Each 30.5- by 30.5-cm test panel was supported on a Type 301 stainless steel frame by three porcelain insulators.

Dissimilar Metal Couples—Panels of Type 304 measuring 20.3 by 30.5 cm were fastened to similarly sized panels of commercially pure metals, copper-base alloys, and nickel-base alloys and exposed for 32 years at the Brackenridge site. The dissimilar metal panels were overlapped by 3 cm and joined by three Type 304 rivets. Duplicate dissimilar metal couple assemblies were exposed in a vertical position and faced directly south. One assembly in each pair was positioned so that the Type 304 panel was below the nonstainless panel in order to expose the stainless steel to the corrosion products of the other panel. Changes in the appearance of the panels in each couple caused by galvanic interaction, corrosion product tarnishing, or individual weathering characteristics are noted in Table 3.

Kure Beach, NC, Site-Groups of 16 samples from 27 different types of stainless steel were exposed facing in a southerly direction at an average distance of 250 m from the normal mean tide level. Half of the specimens in each group were gas tungsten-arc welded without a filler metal. All of the 10- by 15-cm panels were oriented at a 30° angle to horizontal. Pairs of specimens of each stainless type, one welded and one not welded, have been scheduled for exposures of 1, 2, 5, 10, 15, and 20 years. With the exception of 3 alloys, all exposure periods began in the month of June; Type 216, Type 439, and AL-6X[®] (Trademark of Allegheny Ludlum Corporation) alloy were first exposed in August of 1971. As of 1986, all but three of the 27 sample groups

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FIG. 4—An exposure rack at the Brackenridge, PA, atmospheric corrosion testing site.

have been exposed for at least five years; AL 904L[®] (Trademark of Allegheny Ludlum Corporation) alloy, AL-6XN[®] (Trademark of Allegheny Ludlum Corporation) alloy, and Type 441 have only been exposed for two years. The Kure Beach atmospheric test site has been well characterized by extensive long-term tests on stainless steels and other metals, as reported by E. A. Baker in this monograph.

Photometric Testing—A Hunter Associates Laboratory, Inc., Model D-25 sphere colorimeter and color difference meter was used to analyze visible light reflected from the surface of stainless steel specimens. A 20.3-cm-diameter integrating sphere, coated with a white bariumsulfate layer, gathered the specular and diffuse light reflected from a metal specimen and directed it onto a trio of filter-photocell units. The light source-filter-photocell combination was calibrated to approximate a CIE Illuminant C.

The output of the photometric devices consisted of direct color and color difference values measured in terms of a visually meaningful system developed by Judd et al. [17] based on Hering's theory² of color vision. The system can be represented (Fig. 5) as three orthogonal axes representing (1) lightness of color (L units) and (2) the intensity of green or red hues (a units) versus (3) blue or yellow hues (b units). The so-called Hunter a and b values ranged from 0 to ± 99.9 . The Hunter scale for lightness of color ranged in L values from 0 for black to 100 for white. A single-value color scale based on the so-called Judd-Hunter National Bureau of Standards (NBS) unit [17] E for color difference was also used. The magnitude of color difference is described as

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

²Herring theory of color vision: an opponent-colors theory according to which color is due to three pairs of antagonistic processes in the optic system yielding, white and black, yellow and blue, and red and green, respectively [17].

Metals Riveted to Type 304 Stainless	Galvanic	Туре 304	Appearance of
(Composition, wt%)	Attack	Tarnished	Nonstainless Panel
Commercial copper (99.9+ Cu)	no	yes	uniform, light green patina
Commercial aluminum (99+ Al)	no	yes	heavy stain and shallow pitting at edge of panel
Brass (70Cu-30Zn)	no	no	uniform green patina with dark patches
Architectural Bronze (57Cu-42Zn)	no	yes	uniform, green patina with dark patches
Nickel-copper alloy (65Ni-32Cu-2Fe-1Mn)	no	no	brown-matte surface; water marks
Nickel (99+ Ni)	no	no	gray-matte color; water marks
INCONEL ^{®b} alloy 600 (76Ni-15.5Cr-8Fe)	no	no	brown-matte surface; water marks
Commercial lead (99+ Pb)	no	yes	white spots on uniform, gray patina
Commercial tin (99.85+ Sn)	no	yes	pitting on back side ^c of panel
Commercial zinc (99.9+ Zn)	no	no	uniform, light blue-gray patina
Commercial magnesium (99+ Mg)	yes	yes	magnesium panel penetrated along the edge of T-304 panel

 TABLE 3—Dissimilar metal joints with Type 304 stainless exposed for 32 years in a semirural atmosphere.

^aTarnishing of Type 304 attributed to corrosion products from the nonstainless member of each couple. ^bTrademark of the International Nickel Company.

^cFront sides of panels were boldly exposed in a southwesterly direction, and the back sides were partially obstructed by the supporting frame.

L,a,b, COLOR SOLID



The difference indicated by " Δ " was between a given test specimen and a rhodium front faced mirror, which was used as a reference standard (L = 85.5, a = +0.2, and b = +3.0).

Haze values were calculated as the ratio of the amount of diffused light (specular component excluded) to the amount of reflected light (specular component included). The standard rhodium mirror had a haze value of 11.0, which is a nearly perfect mirror (in comparison, a sandblasted surface gives readings close to 100) Specular and diffuse components of reflected light were differentiated by tilting a specimen surface at 8° and 0° angles, respectively, to the incident light beam.

Color measurements were taken on panels of Types 201, 301, 430, and 434 stainless steel before exposure at the Brackenridge site, after 1, 2, 5, 10, and 20 days of exposure, and then at 30-day intervals up to a total of 390 days. Each panel of each grade had one of three surface finishes: No. 2B, Bright Annealed (BA), and Star Brite[®] (Trademark of Allegheny Ludlum Corporation) finish. Before each color measurement, the specimens were gently cleaned in distilled water and dried. The values obtained during the first 20 days did not significantly change relative to measurements made before exposure.

Results and Discussion

Characterization of Brackenridge Test Site

In 1946, Snair [11] reported that the fog, rain, and snow that fell on the test site within the Brackenridge Works of the Allegheny Ludlum Steel Corporation were contaminated by smoke, soot, sulfur dioxide, coal ash, lime, iron, and steam condensation. The 15 stainless grades tested were separated into eight classes of performance based on a subjective visual rating of the degree of corrosion product tarnishing and pitting. The Fe-Cr-Ni austenitic grades that contained more than 18 wt% chromium and 8 wt% nickel (up to 24 wt% chromium and 12 wt% nickel) did not appear to be significantly more resistant to corrosion. Only a Fe-28Cr ferritic and a molybdenum bearing austenitic (Type 316) grade were rated as superior to the 18Cr-8Ni class of stainless.

In 1953 the test site was moved approximately 0.8-km northwest of the Brackenridge steel mill to the Allegheny Ludlum Corporation Technical Center. The relocation of the test site and the deindustrialization of Allegheny River valley have changed the atmospheric test conditions from those described above. The average annual corrosion rates for the commercially pure metals, copper-base alloys, and nickel-base alloys exposed at the Brackenridge site during the last 10 years of a 32-year exposure were (1) consistently greater than the rates reported [18] for 20-year exposures at a rural site and (2) less than those for exposures in industrial and urban locations (Table 2). Consequently, the atmospheric conditions at the Brackenridge test site have been characterized as "semirural."

In addition to the metals used to characterize the Brackenridge test site, 22 grades of stainless steel, a carbon steel, and a weathering steel were also exposed. The average corrosion rate for 15 panels of AISI 1006 sheet over the last 10 years of a 32-year exposure period was $4.25 \,\mu$ m/year. Figure 6 illustrates that a USS COR-TEN A sheet panel gained almost four times as much weight in the first year of exposure (0.097 g/cm²) because of the formation of a protective oxide layer as it had lost during 15 subsequent years (0.025 g/cm²), which amounted to a 14% net weight gain for the weathering steel panel after 16 years in a semirural atmosphere. The gravimetric measurements that have been made annually for the last 10 years of a 32 year period revealed that the weight of the stainless steel specimens had not been reduced in the semirural atmosphere. Only AISI Type 410 showed any significant signs of corrosion product staining because of superficial pitting in the semirural atmosphere.



FIG. 6—Gravimetric measurements for a USS COR-TEN A steel sheet panel during a 16-year exposure in a semirural atmosphere.

Performance of Dissimilar Metal Joints

The appearances of dissimilar metal joints after 32 years in a semirural atmosphere have been noted in Table 3. The joints consisted of Type 304 panels riveted to a variety of commercially pure metals, copper-base alloys, and nickel-base alloys. Type 304 stainless panels were noticeably tarnished by the corrosion products of tin, magnesium, and architectural bronze (Fig. 7). The corrosion products from the copper and aluminum panels only tarnished the Type 304 panels near the joint. The Type 304 panels did not corrode in the semirural atmosphere; consequently none of the other metals were tarnished by the Type 304 stainless. However, the corrosion products that form on 18Cr-8Ni grades of stainless steel in more severe atmospheres have been observed to accelerate localized attack on more highly alloyed stainless grades [6].

The galvanic interaction of copper and aluminum with stainless steel in certain atmospheric applications has been well established [19], but no galvanic corrosion was observed at the Brackenridge site for 619-cm² panels that overlapped in an area of 116 cm^2 . Shallow pitting occurred in a stained region on the boldly exposed, overlapping edge of the commercially pure aluminum panels in contact with Type 304 (staining and pitting did not occur on an uncoupled panel of aluminum that had been exposed under identical atmospheric conditions). The staining on the coupled aluminum panel indicated that water had been retained by deposits in this region for an extended period of time. This was considered to be the primary factor leading to corrosion rather than the galvanic effect that has been reported [20] to cause aluminum screws to pit in stainless steel plates. Severe galvanic attack occurred on the magnesium panels at joints with Type 304. Water had eroded the magnesium in lines of flow on both sides of the panel. Baboian [21] has also reported that Type 304 accelerates the corrosion of magnesium alloys in rural and marine atmospheres.

Performance of Stainless Steels in a Marine Atmosphere

The performance of unwelded stainless steel panels after 5 years in the 250-m lot at Kure Beach, NC, was visually rated, on an arbitrary scale from 0 to 10, based on the degree of corro-



FIG. 7—Appearance of dissimilar metal joints between Type 304 stainless and (a) aluminum—top panel (b) brass—top panel, (c) magnesium—bottom panel, and (d) tin—top panel exposed in a semirural atmosphere for 32 years. Specimen surfaces shown in a, b, and d faced in the direction of the prevailing winds; that shown in c faced in the opposite direction.

sion product staining and the area of sample surface that had been covered by corrosion products (Fig. 8). The degree of corrosion product staining on all of the nonmolybdenum-bearing stainless grades was significant. Performance in the marine atmosphere was directly related to alloy chromium and molybdenum contents (Fig. 9), with two exceptions. The first, Type 216 (typically, in weight percent, Fe-19.75Cr-8.25Mn-6Ni-2.5Mo-0.37N-0.06C) performed slightly better than the high-chromium, ferritic E-BRITE[®] (Trademark of Allegheny Ludlum Corporation) alloy (typically, Fe-26Cr-1Mo) and just as well as the high-nickel, molybdenum-bearing austenitic AL-6X alloy, as shown in Fig. 10. The Type 216 was more resistant to degradation in a marine atmosphere than other austenitic stainless steels of similar chromium and molybdenum contents (for example, Type 316 and Type 317L). The reasons for the exceptional performance of Type 216 may be related to a synergistic effect of chromium and nitrogen, in cooperation with molybdenum [22] or the low level of sulfur [23] in the alloy or both.

The second exception pertained to specimens in the welded condition that were susceptible to preferential corrosion at weld and heat-affect zone surfaces when exposed to the marine atmosphere. Titanium and niobium are used commercially to "stabilize" stainless chemisties in order to avoid the formation of chromium-carbonitrides at grain boundaries [24, 25]. The regions around such precipitates are depleted in chromium, which can "sensitize" a stainless steel to intergranular corrosion and pitting in certain solutions [26, 27]. Compare, for instance, the welded specimens of Type 434 (unstabilized) and Type 439 (stabilized) shown in Fig. 11. The



AISI Type or Alloy Trademark

FIG. 8---Relative degree of corrosion product tarnishing caused by superficial pitting on various grades of stainless steel exposed to a marine atmosphere for five years.



FIG. 9—Appearance of autogenously welded panels of (a) Type 409, (b) Type 304, and (c) Type 316 stainless steel exposed to a marine atmosphere for five years.



FIG. 10—Appearance of autogenously welded panels of (a) E-BRITE alloy, (b) Type 216 stainless, and (c) AL-6X alloy exposed to a marine atmosphere for five years.



FIG. 11—Appearance of autogenously welded panels of (a) Type 434 and (b) Type 439 ferritic stainless steel exposed to a marine atmosphere for five years.

Type 434 was sensitized by the autogenous gas tungsten-arc welding operation and suffered severe intergranular attack and pitting at the weld and heat affected zone while in the marine atmosphere. The weldment in the Type 439 panel was as resistant to corrosion as the base metal. The specified minimum titanium content for Type 439 stainless, circa 1970, was 12 times the carbon content (wt% carbon). Deverell [28] has shown that the lower carbon contents (0.01 to 0.03 wt%) of AOD-refined Type 439 stainless steel (listed as Type 439L in Table 1) required a titanium level greater than $0.2 + 4 \times (wt\% C + wt\% N)$.

Photometric Evaluation of Stainless Steels in the Atmosphere

The chromaticity of light reflected from stainless steel surfaces varies primarily in the intensity of yellow hues; little variation in red-green values is usually detected. For example, brightannealed stainless grades range from +1.5 to +4.8 b units in the following order; Type 434 < Type 430 < Type 301 < Type 201, while a units vary, in no particular order, from -0.3 to -0.75. Both ranges of chromaticity values are close to gray. In general, the stainless grades that appear to be the lightest and the bluest, or least yellow, are usually considered to be the most visually appealing. Subtle changes in the geometric and color attributes of the said grades of stainless steel during a 390-day exposure in a semirural atmosphere were quantified by means of a tristimulus colorimeter. Data obtained for Type 430 stainless specimens with three surface finishes is considered in detail below.

The total color difference measurements for the Type 430 specimens (Fig. 12) indicated that significant change occurred in the appearance of all three surface finishes during exposure to the atmosphere. An analysis of the variables contributing to the total color difference measurements revealed an increase in yellowness (Fig. 13) and a decrease in lightness of color (Fig. 14) with exposure period. Little variation in red-green values was detected (0 to -0.2 a units) for any of the finishes exposed to the atmosphere.

The initial lightness for the Star Brite finish changed from what were considered to be medium (69 to 70 L units) to low values (less than 68 L units) for stainless steel sheet and strip. The lightness values for the 2B and BA finishes were consistently higher than those for the Star Brite finish, but the lightness for all of the finishes decreased at the same rate. The decrease in lightness with continued exposure to the semirural atmosphere describes quantitatively what was visually perceived as a change from a shiny toward a duller/darker surface.

The 2B and BA finishes appeared more yellow (or less gray) than the Star Brite finish. Since



FIG. 12—Total color difference measurements (Judd-Hunter NBS units) for Type 430 stainless steel specimens with cited surface finishes, during a 390-day exposure in a semirural atmosphere.



FIG. 13—Intensity of yellow hues (Hunter +b units) in light reflected from Type 430 stainless steel specimens, with the indicated surface finishes, during a 390-day exposure in a semirural atmosphere.

the hue of the color of a surface is most apparent when viewed at an angle equal to that of the incident light (referred to as the spectral angle), surfaces with strong specular components of reflection appear to have more intense color. However, the increase in yellowness values with the period of exposure for each finish was not associated with an increase in the specular component of reflection, which was demonstrated by relatively consistent haze values (Fig. 15), as discussed below. The yellowing and decrease in lightness of the Type 430 surfaces were attributed to two factors: (1) an increase in the density and distribution of corrosion products, sites of attack and



FIG. 14—Lightness of color measurements (Hunter +L units) for Type 430 stainless steel specimens, with the indicated surface finishes, during a 390-day exposure in a semirural atmosphere.



FIG. 15—Haze measurements for Type 430 stainless steel specimens, with the indicated surface finishes, during a 390-day exposure in a semirural atmosphere.

atmospheric deposits and (2) reported [29] changes in the physical and chemical properties of the stainless steel passive films exposed to the atmosphere. In general, stainless steel surfaces exposed to the atmosphere appear to yellow and darken with age in a manner similar to that of opaque white objects.

Haze measurements revealed differences in the geometric distribution of the light reflected by the three surface finishes. The haze values for the Star Brite finish before and during the exposure period were significantly higher than those for the other finishes (Fig. 15). The Star Brite finish (which consists of a pattern of long, wide, and shallow lines impressed in the rolling direction of a dull BA surface) diffused incident light to a much greater degree than did the smoother 2B and BA finishes. Since the lightness values (Fig. 14) represented the denominator of the ratio defined by the haze values (Fig. 15), the difference in the haze and lightness values for a particular finish and exposure period is inversely related to the intensity of the specular component of reflection. Therefore, the surface finishes, which were the principal factors determining the geometric distribution of reflected light, influenced the measured chromaticity of the specimens. The slightly greater rates of increase in the haze and yellowness values for the 2B and BA finishes relative to the Star Brite finish indicated that, although the degree of attack was similar for all three surfaces, atmospheric degradation was more apparent on the reflective 2B and BA surfaces than on the diffusive Star Brite finish surface.

Conclusions

1. The corrosion resistance of stainless steels in the atmosphere is directly related to alloy chromium and molybdenum contents.

2. Highly alloyed stainless steels, like the 29Cr-4Mo ferritic and 20Cr-24Ni-6Mo austenitic grades, do not pit or suffer corrosion product staining after ten years in a marine atmosphere.

3. Sensitized stainless steel weldments are susceptible to accelerated corrosion in a marine atmosphere.

4. Photometric techniques provide an efficient, reliable, and nondestructive means of quantifying subtle changes in the appearance of stainless steels exposed in the atmosphere. Photometric measurements can be used to evaluate the relative performance of various stainless steel grades and surface finishes in the atmosphere.

5. Severe galvanic corrosion occurs on magnesium panels that are riveted to Type 304 stainless of equal size when exposed to a semirural atmosphere. Type 304 panels in dissimilar metal couples are tarnished by the corrosion products from tin, magnesium, architectural bronze, and to a lesser degree, copper and aluminum.

6. The atmospheric conditions at the Brackenridge, PA, test site have been characterized as semirural.

Acknowledgments

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DISCUSSION

C. A. Cardarelli¹ (written discussion)—How much copper was there in 216 and was molybdenum content biased on the high side to give "very good" corrosion resistance results?

J. R. Kearns, M. J. Johnson, and P. J. Pavik (authors' closure)—AISI Type 216 sheet and strip products typically contain 0.10 wt% copper and 2.5 wt% molybdenum. The material examined in the present study contained 2.61 wt% molybdenum and 0.10 wt% copper. The superior performance of Type 216, relative to AISI 300 series stainless steels of comparable chromium and molybdenum contents (that is, Type 316 and 317), is attributed to the interaction of nitrogen (typically 0.37 wt%) with chromium (typically 19.75 wt%) rather than an increase in the bulk molybdenum content of Type 216. Many studies, beginning with that of Uhlig in 1942, have demonstrated the beneficial effect of nitrogen on the corrosion resistance of austenitic stainless steels; particularly for grades that contained molybdenum. Clayton [I-4] is currently leading an effort toward understanding the mechanism by which nitrogen, molybdenum, and chromium affect the passivity and pitting resistance of austenitic stainless steels in acid and chloride media. Preliminary results indicate that nitrogen may (1) enhance the formation chromium-rich layers in a passive film, (2) directly interact with molybdenum in the passive film, or (3) modify the well known synergism between chromium and molybdenum, or all of the above.

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Long-Term Atmospheric Corrosion Behavior of Various Grades of Stainless Steel

REFERENCE: Baker, E. A. and Lee, T. S., "Long-Term Atmospheric Corrosion Behavior of Various Grades of Stainless Steel," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 52-67.

ABSTRACT: Several grades of stainless steel are evaluated after 26 years of exposure in the marine atmosphere at Kure Beach, NC. The alloys evaluated include 1% Ni + 16% Mn, 5% Ni + Mn, 7 to 10% Ni, 12 to 13% Ni + Mo, 12Cr and 17Cr alloys. The test specimens are in the form of flat panels, with spot welds, arc weldments, and Erickson cup deformations.

An assessment is made of the degree of rust, rust stain, and pitting attack on the boldly exposed surface.

The materials exposed 25 m from the ocean have from 20% rust, 70% rust stain, (Type 316 stainless steel) to 100% rust (Type 410 stainless steel). Surface pitting is insignificant (<0.01 mm) on all material except Type 410 stainless steel, which has surface pits 0.06 mm in depth.

The materials exposed 250 m from the ocean have from 1% rust stain (Types 304 and 316 stainless steels) to 80% rust, 20% rust stain (Type 410 stainless steel), and surface pitting is insignificant.

The spot welded materials have a crevice area between the overlapped surfaces where significant pitting and intergranular corrosion occurs. The attack ranges between 0.08 to 0.17 mm in depth at the 25-m site, and between < 0.01 to 0.10 mm in depth at the 250-m site. Spot weld failure caused by corrosion is found only on Type 430 stainless steel.

The arc welded materials show no evidence of weld failure. The weld and HAZ did have greater rust and rust stain cover than the panel surface.

The materials with Erickson cups show no evidence of stress corrosion failure. However, pitting is more severe in the stressed areas.

KEY WORDS: stainless steels, marine atmosphere, long term corrosion, spot weld, arc weld, Erickson cup, pitting, rust stain, intergranular corrosion

In 1958, the former ASTM Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel, and Related Alloys established a test program to determine the atmospheric behavior of various grades of stainless steel. A set of guidelines were established specifying the types of materials, types of test panels, test panel preparation, and exposure test locations. These guidelines were distributed throughout the industry to supply the test panels needed for test exposure.

Selected materials were removed from atmospheric exposure after three, five, and seven years and tensile evaluations were conducted only after three years. The results of these early evaluations were reported in the ASTM Annual Proceedings of Committee A10 from 1961 to 1969 without any indication of panel appearances.

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Upon the merger of Committee A10 in 1972 with Committee A1 on Steel, Stainless Steel, and Related Alloys, the program was continued with no further documented action until 1984. At that time, the LaQue Center for Corrosion Technology, Inc. (LCCT) initiated an evaluation of the test panels after exposure at its marine atmospheric test site in Kure Beach, NC. With the approval of Committee A1 and Committee G1 on the Corrosion of Metals, test panels were removed and analyzed under the sponsorship of Inco Europe and the Nickel Development Institute.

Experimental Procedure

The materials selected for the atmospheric test program are listed in Table 1 and nominal compositions are given in Table 2. The following guidelines for the preparation of test panels were established:

- 1. flat panels
 - (a) each test panel is $100 \times 356 \times 0.94 \text{ mm} (+1.27, -0.79)$,
 - (b) rolling direction is perpendicular to the 356-mm (14-in.) length, and
 - (c) any one material is from the same heat.

	Material			Туре о	f Panel		
AISI Type	Temper	Finish	Flat	Spot Welded	Arc Welded	Erickson Cup	Supplier ⁴
201	soft	cold rolled	х	х		х	US Steel
201	1/4 hard	cold rolled	Х	• • •			US Steel
201	1/2 hard	cold rolled	Х	• • •			US Steel
201	3/4 hard	cold rolled	Х	Х			US Steel
201	soft	2B		• • •	Х		US Steel
202	soft	cold rolled	Х	х		х	Allegheny Ludlum
16-16-1	soft	cold rolled	Х			х	Allegheny Ludlum
16-16-1	1/2 hard	cold rolled	Х	х			Allegheny Ludlum
301	soft	cold rolled	Х	• • •	•••	х	Allegheny Ludlum
301	1/4 hard	cold rolled	Х	х			Allegheny Ludlum
301	1/2 hard	cold rolled	Х	• • •			Allegheny Ludlum
301	3/4 hard	cold rolled	Х	х	• • •		Allegheny Ludlum
302	soft	cold rolled	Х	х		Х	Republic
302	1/4 hard	cold rolled	Х				Republic
302	soft	2B		• • •	Х		Republic
302	quenched	No. 4	Х	• • •			Republic
302	quenched	No. 7	Х	• • • •	• • •		Republic
304	soft	cold rolled	Х	Х		х	Republic
304	soft	2B		• • •	Х	• • •	Republic
304L	soft	2B		• • •	Х		Armco
316	soft	cold rolled	Х	х	• • •	Х	US Steel
316	soft	2B			Х		US Steel
316L	soft	2B		• • •	Х	•••	Armco
321	soft	2B		•••	Х	• • •	Eastern Rolling
347	soft	2B			Х		Eastern Rolling
410	annealed	No. 2	Х	Х		Х	Crucible
430	soft	cold rolled	Х	Х		Х	Sharon

TABLE 1-Materials used for corrosion evaluation in marine atmospheres.

"Supplier (1) Crucible is now Colt Industries, (2) Republic is now LTV Steel, and (3) Eastern Rolling is now Eastern Stainless Steel.

Stainless					Percer	nt		
Steel Type	Cr	Ni	С	Mo	Mn	N ₂	Fe	Others
201	17	4.5	0.15 max		6.5	0.25	bal	
202	18	5	0.15		8	0.25	bal	
16-16-1	16	1			16		bai	
301	17	7	0.15 max				bal	
302	18	9	0.15 max	• • •			bal	
304	18.5	9.5	0.08 max				bal	
340L	18.5	10.0	0.03 max				bal	
316	17	12	0.08 max	2.25		• • •	bal	
316L	17	13	0.03 max	2.25			bal	
321	18	11	0.08 max				bal	Ti-5x C min
347	18	11	0.08 max				bal	Ti-5x C min
								Cb + Ta - 10x C min
410	12		0.15				bal	
430	17		0.15		• • •		bal	

TABLE 2—Nominal composition for materials (principle elements).

2. spot welded panels

(a) materials are supplied in 100 by 100 mm (+0.25, -0.00) and 100 by 200 mm (+0.25, -0.00) size for spot welding into panels 100 by 356 mm. The identifying code along one side shows the parallel direction of rolling.

3. arc welded panels

(a) materials are welded and sheared into panels 100 by 356 by 3.2 mm (+0.25, -0.13), and

(b) any one material is from the same heat.

4. Erickson cup panels

(a) material are supplied in $76 \times 356 \times 9.4$ mm (±0.25) form,

(b) panels contain three Erickson cups (2 of 80% and 1 of 50% maximum depth) equally spaced along the center line with the small cup in the center. The small cup and one large cup are drilled with a 6.35 mm drill.

5. all panels have test corrosion resisting qualities and pass the boiling nitric acid test (ASTM Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels [A 262]).

All test panels are sent to LCCT where they are sorted and distributed to the following six atmospheric test sites for exposure:

- (1) State College, PA (rural),
- (2) Newark, NJ (industrial),
- (3) Brazos River, TX,
- (4) Battelle, Columbus, OH,
- (5) Kure Beach, NC (marine, 25 m), and
- (6) Kure Beach, NC (marine, 250 m).

Test panels were exposed at the Kure Beach test sites (Fig. 1) during May-Oct. 1958. Scheduled removals were made after three, five, and seven years and the panels were distributed to different participating companies for evaluation. Duplicate test panels were removed from testing at the Kure Beach Test sites in 1984 after 26 years of exposure.



FIG. 1—Views of the atmospheric lots at Kure Beach, NC, where various grades of stainless steel have been exposed for 26 years (1958–1984): TOP: view of 25-mm panels facing east and BOTTOM: view of 250-m lot panels facing south.

An evaluation is made of the percent of each flat surface area (both the side facing skyward and the side facing groundward) that is covered by rust scale and rust stain. Rust is defined as a build-up of corrosion products that is visible on the panel surface at low magnification $(7 \times)$ and has a measurable thickness of 0.05 mm or greater. Rust stain is defined as having no visible corrosion product build-up at low magnification $(7 \times)$. A portion of each panel surface is cleaned (ASTM G1) to remove the rust and rust stain. The surfaces are then examined for pits, and an assessment is made of the pit density as compared to the ASTM Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure (B 537) spot chart (Fig. 2). Depths of pitting are measured with a dial depth gauge.

The spot welded stainless steel test panels are examined for evidence of corrosion in and around the weld area. The five spot welds (6 mm in diameter), which joined two overlapping pieces, are drilled out so the two inner surfaces can be examined (Fig. 3). The crevice surfaces (the area between the overlapped surfaces on the spot welded panels) are measured to determine the depth of pitting and crevice corrosion with a dial depth gauge. Intergranular corrosion was determined by putting a sharp bend (45 to 60°) in the area of a spot weld, then examining this area under 10 to $70 \times$ magnification. Metallographic examinations, needed to verify the depth of intergranular corrosion, are not done.



FIG. 2—Chart for converting percent area defective to rating number.

Results

Results for panels exposed in the 25-m lot after 26 years are given in Table 3 and Fig. 4 and results for those exposed in the 250-m lot are given in Table 4 and Fig. 5. On boldly exposed surfaces, pits are found on Type 410 stainless steel of 0.03 to 0.06 mm in depth and pit depths on all other grades of stainless steel are less than 0.01 mm in depth. The most severe corrosion occurs on the spot welded panels in the crevice area formed by the overlapping sections with a maximum depth of attack of up to 0.22 mm. Pitting attack is found on all material in both the 25 and 250-m lots. Panels exposed in the 25-m lot suffered greater attack. Rust build-up is found and corrosion in the form of pitting, crevices, and intergranular attack occur. Evidence of the attack on Type 316 stainless steel is shown in Fig. 3. Type 430 stainless steel suffers spot weld failure caused by corrosion in the weld heat affected zone in both the 25 and 250-meter lots.

The test panels that had Erickson cups are of Type 201, 202, 16-16-1, 301, 302, 304, 316, 410, and 430 stainless steel. The stressed areas on these materials are examined under $10 \times$ magnification and their is no evidence of cracking. Pit density is much greater on the side of the cup than on the flat surface of the panels. Pit depths are not measured, but appear to be deeper. Metallographic examination would be necessary to identify actual pit depth penetration.



FIG 3—Appearance of spot welded Type 316 stainless steel after 26 years of exposure in the 25-meter atmospheric lot. Rust build up is found in the crevice (top). Pitting and crevice attack (0.14 mm or 0.005 in. minimum, 0.09 mm or 0.003 in. deep on average) are found and intergranular attack is evident in the weld heat affected surface: Top—crevice area before cleaning and bottom—crevice area after cleaning ($\times 2$ magnification).

The test panels that were arc welded were of Type 201, 302, 304, 304L, 316, 316L, 321 and 347 stainless steel. The weld areas on these materials are examined and there is no evidence of weld failure.

Discussion

Corrosion of Stainless Steels in a Severe Marine Environment—25 and 250 M from the Ocean

The 25-m lot is exposed to a very severe marine environment. Annually, chloride ion accumulation can range between 76 042 and 228 125 mg/m^2 and corrosion of high purity iron ranges between 0.2 and 0.6 mm per year [2].

The 250-m test site is a moderate marine environment where the annual chloride accumulation ranges between 21 292 and 60 833 mg/m² [1], and the corrosion rate of high purity wrought iron ranges between 0.04 and 0.09 mm per year [2].³

		ward e	Rust Stain	÷	:	:	80	60	95	70	:	70	:	80	:	<u> </u>	60
	uct d, %	Ground Sid	Rust		:	:	2	ŝ	ŝ	30	:	2	:	20	:	10	20
est lot.	osion Prod Ige on Wel	6	Rust Stain			:	<u> 06</u>	60	95	65	:	6	•	6	:	20	50
tospheric t	Corr Covera	yward Sid	Rust			•	10	S	ŝ	35	:	10		1		80	50
-meter atn		Š	Type Weld	none	none	none	spot	arc	haz	spot	none	spot	none	spot	none	spot	spot
osure in the 25		Side	Pitting Attack ^a	< 0.01/8	< 0.01/5	< 0.01/5	< 0.01/7	< 0.01/6		< 0.01/8	< 0.01/4	< 0.01/6	< 0.01/7	< 0.01/8	< 0.01/8	< 0.01/6	< 0.01/4
ears of expo	e and %	roundward	Stain	5	25	ŝ	10	20		75	02	40	25	50	60	20	20
after 26 ye	ct Coverag el Surface,	3	Rust	Э	ŝ	S	ę	10		S	15	10	20	ę	ς α	ŝ	6
ttainless steels	rrosion Produ Attack on Pan	ide	Pitting Attack ⁴	<0.01/3	< 0.01/3	< 0.01/4	< 0.01/3	< 0.01/6		< 0.01/7	<0.01/3	< 0.01/3	< 0.01/5	< 0.01/4	< 0.01/4	< 0.01/5	<0.01/3
rrosion of s	ů ,	Skyward Si	Rust Stain	55	50	70	70	40		99	35	60	60	70	40	60	40
ILE 3Coi			Rust	45	50	30	30	09		40	65	40	40	30	6 0	40	60
TAE			Condition	cold rolled	1/4 hard	1/2 hard	3/4 hard	2B finish		cold rolled	cold rolled	1/2 hard	cold rolled	1/4 hard	1/2 hard	3/4 hard	cold rolled
			Type SS	201	201	201	201	201		202	16-16-1	16-16-1	301	301	301	301	302

to 0.25%	ie. 8 = 0.	% coverag	= 0 to 0.1	ao pits, 9 =	37-70). 10 = 1	ASTM BS	IT ANSI/	rating (dot cha	it density	h (mm)/p	attack = pit dept	"Pitting
:	100	:	100	spot	< 0.01/4	60	40	< 0.01/3	40	60	cold rolled	430
÷	100	:	100	spot	0.03/0	10	60	0.06/0	:	100	No. 2 finish	410
10	20	6	10	HAZ								
10	5	60	40	arc	< 0.01/5	S	S	< 0.01/5	80	20	2B finish	347
15	6	70	30	haz								
15	40	70	30	arc	< 0.01/8	2	1	< 0.01/6	99	40	2B finish	321
10	1	80	20	haz								
1	1	6	10	arc	< 0.01/8	1	1	< 0.01/8	80	20	2B finish	316L
25	1	60	10	haz								
2	1	6	10	arc	< 0.01/8	1	1	< 0.01/8	95	S	2B finish	316
100	:	100	÷	spot	< 0.01/6	1	1	< 0.01/5	70	20	cold rolled	316
80	20	95	S	haz								
80	20	80	20	arc	< 0.01/7	15	S	< 0.01/6	80	20	2B finish	304L
40	50	75	25	haz								
1	1	15	20	arc	<0.01/4	e G	e	< 0.01/4	95	S	2B finish	304
60	10	60	40	spot	< 0.01/6	30	10	< 0.01/5	80	20	cold rolled	304
:	•••	:	÷	none	< 0.01/7	10	2	< 0.01/5	70	90	No. 7 finish	302
:	:	:	÷	none	< 0.01/6	10	S	< 0.01/3	6	30	No. 4 finish	302
20	10	75	25	haz								
50	50	30	60	arc	< 0.01/7	10	ŝ	< 0.01/4	90	30	2B finish	302
÷	÷	:	:	none	< 0.01/6	50	20	< 0.01/3	60	40	1/4 hard	302

coverage. 7 = 0.25 to 0.5% coverage. 6 = 0.5 to 1.0% coverage. 5 = 1.0 to 2.5% coverage. 4 = 2.5 to 5.0% coverage. 3 = 5.0 to 10.0% coverage. 2 = 10.0 to 25.0% coverage. 1 = 25.0 to 50.0% coverage. 0 = 50% coverage.

	I AE	SLE 4-C0	rrosion of 2	stamless steels	after 20 ye	ars of expo	cz aut ut auso	u-meter all	nospheric	rest tot.		
			Ŭ	orrosion Produ Attack on Pan	ct Coverag	e and %			Corr Cover	osion Prod age on Wel	uct d, %	
			Skyward S	Side	U U	roundward	l Side	Ĩ	cyward Sid	2	Groun Si	dward de
Type SS	Condition	Rust	Rust Stain	Pitting Attack ^a	Rust	Stain	Pitting Attack"	Type Weld	Rust	Rust Stain	Rust	Rust Stain
201	cold rolled	2	20	< 0.01/7	2	25	< 0.01/8	none				:
201	1/4 hard		3 S	< 0.01/8	1	-	< 0.01/6	none	:	:	:	
201	1/2 hard	-	2	<0.01/9	1	2	< 0.01/9	none		:	•	
201	3/4 hard	-	2	<0.01/9	1	3	< 0.01/9	spot	80	20	:	1
201	2B finish	S	10	< 0.01/9	7	7	< 0.01/9	arc	-	95	-	2
								haz	:	30	:	75
202	cold rolled	1	S	< 0.01/8	S	20	< 0.01/8	spot	1	60	-	09
16-16-1	cold rolled	10	80	< 0.01/4	e	50	< 0.01/5	none	:	•	:	:
16-16-1	1/2 hard	9	99	< 0.01/5	ę	30	< 0.01/5	spot	60	10	S	06
301	cold rolled	S	20	< 0.01/8	S	25	< 0.01/8	none	:		•	:
301	1/4 hard	1	2	< 0.01/10	1	2	< 0.01/10	spot	50	50	-	66
301	1/2 hard	1	1	< 0.01/9	1	-	< 0.01/9	none	:	:	:	:
301	3/4 hard	-	1	< 0.01/10	1	1	< 0.01/10	spot	90	10	•	80
302	cold rolled	ę	4	< 0.01/7	ŝ	20	< 0.01/8	spot	95	S	1	40

. 250 4 36 Ś TABLEA

1 to 0.25%	te. 8 = 0.	% coverag	= 0 to 0.1	to pits, 9	(37-70), 10 = 1	ASTM BS	urt ANSI/	rating (dot cha	ou o	h (mm)/r	attack = nit dent	"Pitting
•	10	10	6	spot	< 0.01/7	65	10	< 0.01/8	80	20	cold rolled	430
:	100	:	100	spot	0.01/1	30	65	0.01/1	20	80	No. 2 finish	410
95	S	95	S	haz								
95	S	95	S	arc	< 0.01/8	S	2	< 0.01/7	10	S	2B finish	347
ŝ	10	:	75	haz								
4	•	:	100	arc	< 0.01/10	S	ŝ	< 0.01/8	S	ŝ	2B finish	321
7	•	÷	••••	haz								
	:	80	1	arc	< 0.01/10	1	0	< 0.01/10	-	0	2B finish	316L
•	10	:	15	haz								
10	10	10	10	arc	< 0.01/9	1	0	< 0.01/9	Т	0	2B finish	316
06	:	-	÷	spot	< 0.01/9	1	-	< 0.01/9	1	1	cold rolled	316
85	S	10	10	haz								
50	•	25	75	arc	< 0.01/9	15	10	< 0.01/9	10	2	2B finish	304L
25	S	20	80	haz								
:	100	:	100	arc	< 0.01/9	20	S	< 0.01/8	40	S	2B finish	304
Ι	:	60	:	spot	< 0.01/9	1	1	< 0.01/9	1	1	cold rolled	304
:	•	••••	:	none	< 0.01/9	ŝ	1	< 0.01/8	2	-	No. 7 finish	302
:	;	:	:	none	< 0.01/8	20	ŝ	< 0.01/7	10	2	No. 4 finish	302
	30	:	20	haz								
:	100	:	100	arc	< 0.01/9	S	1	< 0.01/9	10		2B finish	302
:	••••	:	÷	none	< 0.01/8	4	2	< 0.01/8	4	2	1/4 hard	302

ъ° coverage, 7 = 0.25 to 0.5% coverage. 6 = 0.5 to 1.0% coverage. 5 = 1.0 to 2.5% coverage. 4 = 2.5 to 5.0% coverage. 3 = 5.0 to 10.0% coverage. 2 = 10.0 to 25.0% coverage. 1 = 25.0 to 50.0% coverage. 0 = 50% coverage.

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FIG. 4-Relative performance of stainless steels exposed 25 m from the ocean for 26 years.

Type 201 Stainless Steel

25-Meter Lot-Type 201 stainless steel (cold-rolled, 1/4, 1/2, and 3/4 hard) is 30 to 50% covered with rust, with the balance of the surface covered by rust stain. Panels in the 1/2 and 3/4 hard conditions show the greater resistance to rust coverage. The pits were <0.01 mm deep and pit density on all the Type 201 material tested is very similar and rated either three or four (5 to 10% of the area pitted).

Spot-welded Type 201 (3 /4 hard cold rolled) stainless steel has a slight rust build-up in between the two plates. Many pits (0.15 mm maximum, 0.12 mm average are scattered over the crevice area. Intergranular corrosion occurs in the weld heat affected zone (HAZ) of the weld and base metal.

250-Meter Lot-Type 201 stainless steel (cold-rolled) is 2% covered by rust spots and 20% by rust stain, while Type 201 under the other conditions ($^{1/4}$, $^{1/2}$, and $^{3/4}$ hard) is 1% covered by rust spots and 2% by rust stain. The pits were <0.01 mm in depth and pit densities are rated seven (0.50 pitted area) for cold rolled, eight (0.25 pitted area) for $^{1/4}$ hard, and nine (0.1 pitted area) for $^{1/2}$ and $^{3/4}$ hard. Type 201 (2B) is 5% covered by rust, 15% by rust stain and had pits <0.01 mm in depth and a pit density is rated nine (0.1% pitted area).

Spot welded Type 201 (3/4 hard) stainless steel has some rust build-up in a localized area in

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FIG. 5-Relative performance of stainless steels exposed 250 meters from the ocean for 26 years.

between the two plates. Pitting (0.08 mm maximum, 0.07 mm average in depth) is found just under the overlapping edge of the crevice. Intergranular corrosion is found in the weld HAZ.

Type 202 Stainless Steel

25-Meter Lot-Type 202 stainless steel (cold-rolled) is 40% covered by rust and 60% covered by rust stain. The pits are < 0.01 mm in depth and pit density is rated seven (0.5% of the pitted area).

Spot-welded Type 202 (soft cold rolled) stainless steel has slight rust build-up in between the two plates. Very many pits (0.21 mm maximum, 0.17 mm average in depth) are scattered over the crevice area. Severe intergranular corrosion is found in the weld, weld HAZ, and base metal.

250 Meter Lot-Type 202 stainless steel (cold rolled) is 1% covered by rust spots, 5% by rust stain. The pits are < 0.01 mm in depth and pit density is rated eight (0.25% of the pitted area).

Spot-welded Type 202 (soft cold rolled) stainless steel has very little rust in between the two plates. Pitting (0.04 mm maximum, 0.003 mm average in depth) is found in the crevice area;
most of the pits are located along a fine line just under the overlapping pieces. Intergranular corrosion is found in the weld HAZ.

16CR-16Mn-1Ni

25-Meter Lot-16Cr-16Mn-1Ni stainless steel (cold-rolled, $\frac{1}{2}$ hard) is 40 to 65% covered by rust and the balance covered by rust stain; the pits are <0.01 mm in depth and pit density is rated three (10% pitted area).

Spot-welded 16-16-1 ($\frac{1}{2}$ hard) stainless steel has rust build-up (0.30 mm) in between the two plates. Very severe pitting (0.22 mm maximum, 0.17 mm average) is found in the crevice area. Intergranular corrosion is found in the weld, weld HAZ, and base metal.

250 Meter Lot-16Cr-16Mn-1Ni stainless steel (cold rolled and 1/2 hard) is 6 to 10% covered by rust spots, 70 to 90% by stain. The pits are < 0.01 mm in depth and pit density is rated four and five for the two conditions, respectively (with 2.5 and 5% pitted area).

Spot-welded 16-16-1 ($\frac{1}{2}$ hard) stainless steel has rust build-up (0.10 mm thick) in between the two plates. Pitting (0.06 mm maximum, 0.04 mm average in depth) is found in the crevice area.

Type 301 Stainless Steel

25 Meter Lot-Type 301 stainless steel (cold-rolled, 1/4, 1/2 and 3/4 hard) is 30 to 60% covered with rust and the balance covered by rust stain. Panels in the 1/4 hard condition show greater resistance to rust coverage. Pits are <0.01 mm in depth and pit density for all Type 301 panels is very similar and rated either four or five (with 2.5 to 5% pitted area).

Spot-welded Type 301 ($^{1}/_{4}$ hard) stainless steel has slight rust build-up in between the two plates. Many pits (0.18 mm maximum, 0.15 mm average in depth) are scattered over the crevice area. A line of pits is located along the edge of the overlapping pieces. Intergranular corrosion occurs in the weld HAZ, weld, and base metal.

Spot-welded Type 301 (3 /4 hard) stainless steel has slight rust build-up in between the two plates. Many pits (0.12 mm maximum, 0.09 mm average in depth) are scattered over the crevice area. Also, a line of pits (0.02 to 0.06 mm in depth) is located along the edge of the overlapping pieces. Intergranular corrosion occurs in the weld HAZ, weld, and base metal and the attack is evident on the outside surface of the panels.

250 Meter Lot-Type 301 cold-rolled stainless steel is 5% covered by rust spots and 10% by rust stain, while the other Type 301 stainless steels ($^{1}/_{4}$, $^{1}/_{2}$, and $^{3}/_{4}$ hard) are 1% covered by rust spots and 1 to 2% covered by rust stain. The pits are <0.01 mm in depth and the pit densities are rated eight (0.25% pitted area) for the cold-rolled material, nine (0.1% pitted area) for the $^{1}/_{2}$ hard material, and ten (0% pitted area) for the $^{1}/_{4}$ and $^{3}/_{4}$ hard material.

Spot-welded Type 301 ($^{1/4}$ hard) stainless steel has rust stain in between the two plates. Pitting (0.09 mm maximum, 0.07 average in depth) is found under the crevice and in the weld HAZ.

Spot-welded Type 301 (3 /4 hard) stainless steel has rust stain in between the two plates. Very few small pits (0.01 mm in depth) are found at the edge of the overlap. Pits (0.01 mm in depth) are found in the weld HAZ.

Type 302 Stainless Steel

25-Meter Lot-Type 302 stainless steel (cold-rolled, 1/4 hard, soft 2B, #4 and #7) is 30 to 60% covered by rust, with the balance covered by rust stain. Panels in the soft 2B and quenched annealed to the #4 and #7 conditions show greater resistance to rust coverage. The pits are <0.01 mm in depth and pit density is rated between three and five (with 2.5 to 10% pitted area).

Spot-welded Type 302 (soft cold-rolled) stainless steel has slight rust build-up in between the

two plates. Many pits (0.20 mm maximum, 0.15 mm average in depth) and some locally corroded areas (0.02 to 0.04 mm in depth) are evident. Intergranular corrosion occurs in the weld HAZ, weld, and base metal.

250 Meter Lot-Type 302 stainless steels (cold-rolled, $\frac{1}{4}$ hard and $\frac{47}{7}$) are 1 to 3% covered by rust spots and 2 to 4% covered by rust stain. The pits are <0.01 mm in depth and the pit density is rated seven and eight (with 0.25 to 0.5% pitted area). The other Type 302 steels (#4 and 2B finish) are 1 to 2% covered by rust spots, 10% covered by rust stain. The pits are <0.01 mm in depth and pit density is rated seven to nine (with 0.1 to 0.5% pitted area).

Spot-welded Type 302 (soft cold-rolled) stainless steel has rust stain in between the two plates. A few very small pits (0.01 mm in depth) are found at the edge of the overlap. Pits (0.01 mm in depth) are found in the weld HAZ.

Type 304 Stainless Steel

25 Meter Lot-Type 304 stainless steel (cold-rolled) is 20% covered by rust with the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density rating is five (2.5% pitted area). Type 304 stainless (soft 2B) is 5% covered by rust with the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density is four (5% pitted area). Type 304L stainless steel (soft 2B) is 20% covered by rust with the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density is four (5% pitted area). Type 304L stainless steel (soft 2B) is 20% covered by rust with the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density is rated six (1% pitted area).

Spot-welded Type 304 (soft cold-rolled) stainless steel has slight rust build-up in between the two plates. Very many pits (0.10 mm maximum, 0.08 mm average in depth) are found in the crevice area. Intergranular corrosion is found in the weld and weld HAZ.

250 Meter Lot-Type 304 stainless steel (cold-rolled) is covered by 1% rust spotting and 2% staining. Its pits are <0.01 mm in depth and they had a pit density of eight (0.25% pitted area). Type 304 (2B) is 5% covered by rust spots and 40% covered by rust stain. The pits are <0.01 mm in depth and the pit density is rated eight (0.25% pitted area). Type 304L (2B) is 2% covered with rust spots and 10% covered by rust stain. The pits are 0.01 mm in depth and pit density is rated nine (0.1% pitted area).

Spot-welded Type 304 (soft cold rolled) stainless steel has slight rust and rust stain in between the two plates. Pits (0.06 mm maximum, 0.04 mm average in depth) are scattered in the crevice area and pits occur in the weld HAZ.

Type 316 Stainless Steel

25 Meter Lot-Type 316 stainless steel (cold-rolled) is 20% covered by rust and 70% covered in rust stain. The pits are <0.01 mm in depth and pit density is rated five (2.5% pitted area). Type 316 stainless steel (2B) is 5% covered with rust and 50% covered by rust stain. The pits are 0.01 mm in depth and pit density is rated eight (0.25 pitted area). Type 316L stainless steel (soft 2B) is 20% covered by rust and the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density is rated eight (0.25% pitted area).

Spot-welded Type 316 (soft cold rolled) stainless steel has slight rust build-up in between the two plates. Many pits (0.14 mm maximum, 0.09 mm average in depth) are scattered over the crevice area. Intergranular corrosion is found in the weld and weld HAZ.

250-Meter Lot-Type 316 stainless steel (cold-rolled) is 1% covered by rust spots and 1% by rust stain, while the 2B material has no rust spotting and only 1% rust stain coverage. The pits are <0.01 mm in depth and the pit density is rated nine (0.1% pitted area). Type 316L (2B) has no rust spots with only 1% coverage in rust stain. No pits are visible on the surface and the pit density is rated ten (0% pitted area).

Spot-welded Type 316 (soft cold-rolled) stainless steel has slight rust stain in between the two

plates. Several small pits (0.01 mm in depth) and a small crevice corrosion site (0.01 mm in depth) are found. Intergranular corrosion is found in the weld HAZ.

Type 321 Stainless Steel

25-Meter Lot-Type 321 stainless steel (2B) is 40% covered by rust and the balance covered in rust stain. The pits are <0.01 mm in depth and the pit density is rated six (1% pitted area).

250 Meter Lot-Type 321 stainless steel (2B) is 5% covered by rust spots and 5% covered by rust stain. The pits are 0.01 mm in depth and the pit density is rated eight (0.25% pitted area).

Type 347 Stainless Steel

25-Meter Lot-Type 347 stainless steel (2B) is 40% covered by rust and the balance covered in rust stain. The pits are <0.01 mm in depth and the pit density is rated six (1% pitted area).

250 Meter Lot-Type 347 stainless steel (2B) is 5% covered by rust spots and 10% covered by rust stain. The pits are < 0.01 mm in depth and the pit density is rated seven (0.5% pitted area).

Type 410 Stainless Steel

25 Meter Lot-Type 410 stainless steel (Annealed #2) is 100% covered with rust. The pits are 0.06 mm in depth and the pit density is rated zero (50% pitted area).

Spot-welded Type 410 stainless steel (annealed) has rust build-up (0.10 to 0.30 mm) in between the plates. Many pits and crevices (0.19 mm maximum, 0.15 mm average in depth) are scattered over the crevice area. Intergranular corrosion is evident in the weld HAZ.

250 Meter Lot-Type 410 stainless steel (annealed #2) is 80% covered by rust and 10% covered by rust spots. The pits are 0.01 mm in depth and the pit density is rated one (50% pitted area).

Spot-welded Type 410 (annealed) stainless steel has rust in between the two plates. Many pits (0.15 mm maximum, 0.01 mm average in depth) is found in the crevice area. Intergranular corrosion is found in the weld and weld HAZ.

Type 430 Stainless Steel

25 Meter Lot-Type 430 stainless steel (cold-rolled) is 60% covered by rust and the balance covered by rust stain. The pits are <0.01 mm in depth and the pit density is rated three (10% pitted area).

Spot-welded Type 430 stainless steel (cold-rolled) have rust build-up (0.10 to 0.30 mm) in between the two plates. Many pits (0.16 mm maximum, and 0.12 mm average in depth) are scattered over the crevice area. The spot welds can be broken under slight bending pressure leaving a mound area on one side and a depression on the other side. This separation line followed the weld/weld HAZ interface.

250 Meter Lot-Type 430 stainless steel (cold-rolled) is 20% covered by rust and 80% covered by rust stain. The pits are < 0.01 mm in depth and the pit density is rated eight (0.25% pitted area).

Spot-welded Type 430 (soft cold-rolled) stainless steel has rust in between the two plates. A few pits (0.12 mm maximum, 0.05 mm average in depth) are found in the crevice area. The spot welds are broken easily under slight bending pressure, leaving a mound area on one side and a depression on the other side. The separation line follows the weld/weld HAZ interface.

Summary

All of the stainless steels evaluated in this program exhibit excellent resistance to corrosion over the 26 year exposure in marine atmospheres. Insignificant pitting (< 0.01 mm) is measured

on the boldly exposed surfaces of all materials except Type 410 stainless steel which showed pitting to only a slightly greater degree (a maximum of 0.06 mm).

All of the stainless steels exhibit rust staining and rust coverage to varying degrees. This is more extensive in the 25-m test lot nearest the ocean as compared to the 250-m test lot. In the 25-m lot exposures, Types 304 and 316 stainless steels generally exhibit the least rust coverage. In the 250-m test lot, all of the 200 and 300 series stainless steels show less than 50% rust staining and only minimal rust coverage.

The spot-welded stainless steels had a crevice area in between where the two plates overlapped 2.5 cm (25.5 cm²). In this crevice area, significant pitting and intergranular corrosion is observed. In the 25-m lot, the average attack on the ten stainless alloys is from 0.08 mm to 0.17 mm. In the 250-meter lot, the average attack on the ten stainless alloys is from < 0.01 to 0.10 mm. Type 430 stainless steel does suffer spot welded failures in both the 25 and 250-m lots because of the corrosion of the weld.

All the arc welded stainless steels exposed show no evidence of weld failure.

All stainless steels with Erickson cups exposed show no evidence of stress corrosion failure in the stressed areas. There are a great many more pits visible on the side of the Erickson cup than are found on the flat surface of the test panel exposed in the 25-meter lot.

Acknowledgement

The authors acknowledge the help of Mr. Jack Lewis, who exposed the panels, recorded data for 26 years, and assisted in the evaluation.

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DISCUSSION

H. H. Lawson¹ (discussion questions)—Your original program included tensile evaluations. Were such tests made on the 26-year samples?

Also, loaded and unloaded springs were included. Were these included in the current program?

E. Baker (author's closure)—Tensile evaluations were not performed on the 26-year samples. It is our hope this can be done at some future date.

Loaded and unloaded springs are still exposed at Kure Beach. No evaluations were made on the loaded and unloaded springs exposed there.

Atmospheric Corrosion and Development of a Stainless Steel Alloy Against Marine Environments

REFERENCE: Ito, S., Omata, H., Murata, T., and Yabumoto, Y. "Atmospheric Corrosion and Development of a Stainless Steel Alloy Against Marine Environments," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 68-77.

ABSTRACT: In order to investigate atmospheric corrosion of stainless steel, exposure tests were carried out at several locations. By analysis of the test results, it is considered that the distance from the shoreline can be the most significant factor affecting corrosion. Utilizing a developed evaluation method in laboratory and exposure tests, a new alloy of ferritic stainless steel as bright annealed surface was developed, based on the finding that amorphous silicon oxide film is more corrosion resistant against marine atmosphere. The proposed alloy is a type of highly purified 19% chromium ferritic stainless steel covered with a corrosion resistant bright annealed surface film.

KEY WORDS: atmospheric corrosion, stainless steels, bright annealing, passive film, silicate, surface analysis, electrochemistry

Stainless steels have been widely used for exterior applications in architecture, automobiles, and trains on account of corrosion resistance and aesthetic appeal of the surface. However, the surface is sometimes damaged by spotty rusting from atmospheric corrosion after long-time exposure to severe environments, particularly marine seashore, although the corrosion of steel substrates is much less than that of carbon steel and low alloyed steels. This type of atmospheric corrosion of stainless steels has been investigated by several researchers [1-4]. However, the data on corrosion of bright annealed surface of stainless steel were not well established in spite of its shiny appearance. Therefore, a series of studies on atmospheric corrosion of stainless steels was carried out in order to clarify the morphology of corrosion and the environmental factors significantly affecting the corrosion. Then, a bright annealed ferritic stainless steel resistant to atmospheric corrosion was developed, based on a finding of a resistant surface film.

Procedure

Exposure Test

The specimens, 0.5 by 60 by 300 mm in size, were placed horizontally on the exposure test panels located around the Tokyo Bay area of Japan at different distances from the shoreline. Exposure in the horizontal position was assumed to give the severest condition for corrosion. After one- to three-months exposure, the specimens were cleaned and gently rubbed in running

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water, and then the rating score of the residual aesthetic appeal was assigned by comparison with the standard specimens. The rating score increases with increasing corrosion resistance. The rating score "0" means all the surface is covered by red rust, whereas "10" means no rust is apparent with almost the same appearance as before the exposure. The tests were conducted several times through summer or winter, because the severity of the environment changes with the season.

Specimens

Bright annealed American Iron and Steel Institute (AISI), 304, 434, and 430 stainless steels were utilized in addition to the newly developed bright annealed ferritic stainless steels containing 19% chromium with additions of copper and niobium as shown in Table 1. Two to twenty percent chromium iron base high purity alloys were also used in some cases to examine the effect of chromium content on the ability of air formed films to heal a scratched bright annealed film.

Electrochemical Experiments

In order to understand how fast the air formed film grows on the stainless steels containing various chromium contents, potential decay curves were obtained in deaerated 0.1 N sodium chloride (NaCl) buffer solution after the stainless steels were polished with #600 grit emery paper in ethanol, and stored in decicator for a given period (1 h to 3 weeks).

Surface Analysis

The chemical composition of the outermost surface films and their depth profile were obtained by Auger electron spectroscopy (AES). The structure of the surface films were investigated mainly by reflection electron diffraction with the accelerating voltage, 150 kV. Nonmetallic inclusions and precipitates at the surface of steel sometimes play a role of defects initiating rusting, so that they were at times observed by transmission electron microscopy of the extraction replicas.

In addition, the DC electrical resistance of the surface film on the stainless steels was obtained by a conventional SQ meter (produced by Yamasaki Seisakusho) by measuring the film resistance between sliding carbon rod and metal substrate.

Results and Discussion

The morphology of atmospheric corrosion (Fig. 1) shows typical surface appearance of rusted stainless steel of AISI 304 and 430 exposed in the distance of 5 m from seashore for three months. The spotty rust reduces the aesthetic appeal of stainless steel severely. There were two types of corrosion morphology observed on the surface shown in Fig. 2. One was caused by

Sample	С	Si	Mn	P	s	Ni	Cr	Cu	Nb
	0.011	0.51	0.11	0.025	0.004	0.32	19.44	0.44	0.43
В	0.015	0.47	0.17	0.025	0.001	0.27	19.43	0.40	0.35
С	0.015	0.30	0.14	0.024	0.006	0.26	19.36	0.44	0.38

TABLE 1-Examples of chemical composition of developed stainless steel, ppm.

Note: 90 < N < 170 ppm and 30 < O < 60 ppm.



FIG. 1—Appearance of rusted AISI 304 (left) and AISI 430 (right) stainless steel surface exposed in the distance of 5 m from the shoreline for three months.



FIG. 2—Two types of damage by rusting (a) pitting (b) film dissolution: (a) developed steel (Sample A) exposed at 5 m from the shoreline for one month and (b) AISI 430 steel exposed at 5 m from the shoreline for one month.

pitting corrosion (Fig. 2a), the diameter of which varied from 5 to 200 μ m. The other appeared to be damaged by the surface film dissolution consequently disclosing the substrate grains underneath (Fig. 2b). The reason for existence of the two types of corrosion morphology may be closely related to the chemical performance of the film. With a highly corrosion resistant film of silicate (SiO₂) described later, the damage tended to mainly be pitting corrosion rather than film dissolution.

The Environmental Effect

In order to understand the effect of the environment on the corrosion of bright annealed stainless steels, the stainless steel specimens having a variety of chemical compositions and surface films were exposed. The typical results were shown in Fig. 3, where the distance from the shoreline has a significant effect on the atmospheric corrosion of stainless steels. That is, the closer to the shoreline, the more the corrosion occurred, resulting in the wider statistical distribution of rating scores dependently on the steel and its surface chemical composition. In mild environments, such as locations far from the shoreline, there are no differences in corrosion resistance among various types of stainless steel as shown in Fig. 4a. Even AISI Type 304 and 430 did not change in corrosion resistance as shown in the results of another run of exposure tests in Fig. 4b. On the contrary, the severe environments at the seashore showed differences in corrosion of stainless steel is mostly caused by chloride attack from marine environments.

Based on the results of the environmental tests showing the corrosion described so far, a quantitative method simulating atmospheric corrosion under chloride attack was developed to evaluate the corrosion resistance of stainless steel in the laboratory. The details of the experimental method have been reported elsewhere [5]. Through this method, one can identify what types of surface may be the most resistant to corrosion, and then develop a new type of stainless steel alloy, although exposure tests were also necessary to assure that the performance was as expected.

Effect of Alloy Elements

Stainless steels have been commercially produced in varieties of surface finishes such as bright annealed, acid pickled, and mechanically polished finish. In the present paper, bright annealed ferritic stainless steel was examined from the view point of what composition and structure of bright annealed film is resistant against atmospheric corrosion. The bright annealed film generally consists of oxides of silicon, chromium, and iron, as shown in Fig. 5 of



FIG. 3—Corrosion resistance rating distributions at the distance (a) 6 km, (b) 1 km, (c) 5 m from the shoreline (the first exposure test).



FIG. 4—Corrosion resistance rating of different types of stainless steel when exposed to (a) a severe environment and (b) a mild environment for four weeks (the fourth exposure test).



FIG. 5—Typical depth profile of bright annealed surface by AES measurement (1 min of sputtering time is approximately correspondent to 80 A of thickness).

AES depth profile. The chemical composition of the film strongly depends upon the bright annealing conditions and steel compositions. Through laboratory and exposure tests, it was found that the more silicon enriched in the surface film, the more resistant the alloy was to corrosion. Figure 6 is a typical result indicating the relationship between the amount of silicon in the film and the rating score of exposure tests at the seashore. With more than 20 to 30 at% of silicon in the outermost surface, the film is considered to mostly consist of SiO₂. The result of reflection electron diffraction revealed the film structure was amorphous as indicated by halo pattern in Fig. 7. Therefore, amorphous SiO₂ film can give steel highly corrosion resistant surface to marine atmospheres. It is considered that up to certain amount of silicon content in the steel may be necessary to produce a stable SiO₂ film on the surface during the bright annealing process. The silicon content in surface film may be varied by the silicon content in steel and the bright annealing conditions. Therefore, stainless steel specimens with a range of silicon content



FIG. 6—Relationship between corrosion resistance rating scores of exposure test specimens and amount of silicon contained in the surface film.



FIG. 7-Reflection electron diffraction pattern obtained from silicon enriched surface film.

were bright annealed under the same condition, although the amount of silicon in steel was not changed greatly because loss of mechanical workability would occur. Even so, the exposure test as shown in Fig. 8 gave the results describing that the higher the silicon content in the steel, the higher the corrosion resistance tended to be.

In order to understand why silicon oxide films are resistant to corrosion, the electrical resistance of the film was examined by a conventional SQ meter. Figure 9 is an example of the data in which the electrical resistance of the film became higher with an increase in silicon enriched at the surface. The insulative SiO₂ film is considered to retard corrosion current flow, even if the corrosion initiates. And in addition, it is not unreasonable to think that the covalent bonds of SiO₂ may be more difficult to break through chloride attack than the ionic bonds of chromium oxide, which generally formed on a bright annealed surface.

However, once broken, the SiO_2 film is not capable of healing defects automatically. With the existance of some defects in the bright annealed film, the substrate metal is directly exposed to



FIG. 8—Corrosion resistance rating score of exposure test specimens of stainless steels containing various amounts of silicon in steel (Steel A: 0.51 silicon, Steel B: 0.47 silicon, Steel C: 0.30 silicon at the third exposure test).



FIG. 9—Relationship between surface film electrical resistance and amount of silicon contained in surface film.

air and then, the air formed film will grow depending upon the chromium content of steel. To understand the behavior of the air formed film, the potential decay curves of the polished steels with various chromium content were obtained in 0.1 M NaCl solution.

The obtained results are shown in Fig. 10, where the specimens were stored in desiccator for one week after polishing in ethanol. The steels containing higher chromium contents in the alloy exhibited longer potential decay times. The behavior of 15 and 20% chromium steels is quite



FIG. 10—Potential decay curves of air formed film grown on 2 to 20% chromium bearing steel (one-week stored in desiccator after polishing).

different from the steel containing less chromium in that they undergo gradual self repassivation after the partial breakdown of the air formed film. In addition, the longer storage time led to higher stabilization of air formed film.

Figure 11 shows the results of AES surface analysis of 5% chromium steel and 15% chromium steels along with various storage times, that is 1 h, 1 day, and 1 week. It is interesting to note that the longer storage time enhances chromium enrichment in the surface films together with their thickness. This observation indicates that the steel with more than 15% chromium keeps its film stability.

The nonmetallic inclusions, precipitates in steel and grain boundaries sometimes produce defects in the surface film, where the localized corrosion easily initiates. Particularly, manganese sulfide (MnS) has been reported to initiate corrosion [6]. However, with a low level of sulfur, large MnS deteriorating corrosion resistance usually does not occur according to reports to date [7,8]. Even so, the lower contents of manganese and sulfur in steels are desirable to reduce defect levels. Furthermore, the composition of MnS can be made insoluble by copper



FIG. 11-Results of AES depth profile for 15% chromium steel with various storage time in desiccator.



FIG. 12—Scanning electron microscopy and energy dispersive X-ray spectra of complex sulfide inclusion modified by copper addition in stainless alloy.

additions as is evident in Fig. 12, where MnS was converted to the more water insoluble complex compounds, such as (Mn,Cu)S.

From the concept discussed so far, a ferritic stainless steel alloy resistant to atmospheric corrosion was developed. An example of its chemical composition is shown in Table 1. The steel is a type of highly purified 19% chromium ferritic stainless steel with additions of copper and niobium. A bright annealed surface finish on this steel gave superior corrosion resistance in marine atmospheres, as shown in Fig. 4.

Conclusion

In order to investigate the atmospheric corrosion of stainless steels, exposure tests were carried out at several locations. By analysis of the test results, it was found that the distance from the shoreline was the most significant factor affecting the corrosion. The further from the shoreline, the less the corrosion occurred.

Utilizing an evaluation method in laboratory and exposure tests, a new ferritic stainless steel alloy with a bright annealed surface was developed, based on the finding that an amorphous silicon oxide film is more corrosion resistant in marine atmospheres. The alloy is a type of highly purified 19% chromium ferritic stainless steel with additions of copper and niobium.

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DISCUSSION

Robert Baboian¹ (written discussion)—Your results show the new alloy has improved corrosion resistance over Type 434 stainless steel. However, the addition of 1% molybdenum in 434 stainless steel (SS) provides resistance to localized corrosion by repassivation. If the surface film is scratched on the new alloy, does repassivation occur as it does with 434 SS?

Ito et al. (authors' closure)—According to surface analysis of passive film, addition of molybdenum promotes chromium enrichment into the passive film, leading to high capability for passivation and repassivation. One percent molybdenum addition is approximately correspondent to 1 to 2% chromium addition in terms of chemical composition of passive film. The developed steel (19% chromium) contains 2% more chromium than AISI 434 (17% chromium with 1% molybdenum). It can be considered that both steels exhibit comparable performance in passivation and repassivation, although a scratch test was not carried out. In addition, the new steel contains copper and niobium, which is thought to help the steel passivate. Every exposure test resulted in the improved corrosion resistance of the new alloy over AISI 434 stainless steel. (See Ref 1).

C. A. C. Cardarelli² (written discussion)—(1) Is developed alloy manufactured by AOD melting? (2) Is there other degassing? (3) Is the Japanese Standards SUS (AISI) number designated?

Ito et al. (authors' closure)—The developed alloy is mainly manufactured by vacuum oxygen decarborization (VOD) process. This process also includes desulfurization and degassing simultaneously with a special treatment.

The alloy is not designated by Japanese Standards (SUS) number, but designated by Nippon Steel Co's own number to be available on commercial market.

A. Raman³ (written discussion)—Compare your disk with those of ferritic stainless steels containing aluminum (aluminum-content and so forth).

Ito et al. (authors' closure)—The developed steel presented here is mostly used as bright annealed finish. Considering bright annealing process in mixed gas of nitrogen and hydrogen, aluminum could be oxidized to be more enriched at the surface than silicon. Aluminum oxide film formed by the annealing process tends to carry too much defect by incorporating other elements, chromium, iron, and so forth, to give corrosion resistance. Therefore, aluminum content in the new alloy was reduced to a trace amount to obtain stable SiO₂ film, which is more corrosion resistant.

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Lawrence E. Eiselstein¹ and Robert D. Caligiuri¹

Atmospheric Corrosion of the Suspension Cables on the Williamsburg Bridge

REFERENCE: Eiselstein, L. E. and Caligiuri, R. D., "Atmospheric Corrosion of the Suspension Cables on the Williamsburg Bridge," *Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 78-95.

ABSTRACT: The Williamsburg Suspension Bridge across the East River in New York City was opened to traffic in 1903. The four main support cables are composed of 7696 high carbon steel wires spun into 470-mm diameter cables. These wires were ungalvanized but given a protective organic coating when installed. The cables were inspected in 1980 and found to have undergone a significant amount of atmospheric corrosion. In 1982, wire samples up to 91 m in length were removed from the cables and the extent of atmospheric corrosion damage was evaluated. Mechanical properties experiments on corroded and uncorroded wires indicate that the atmospheric induced corrosion damage has degraded the load bearing capacity of the cable. An accelerated cyclic wetting/drying atmospheric corrosion test was used to estimate the current rate of corrosion induced damage. Based on these observations, it was concluded that the acidity and the chloride ion content in the New York City area precipitation, plus the graphite in the original organic coating, are the principal factors contributing to the atmospheric corrosion of the cable. Furthermore, the estimated current rate of corrosion confirms that some sort of cable rehabilitation or replacement is necessary.

KEY WORDS: Williamsburg Bridge, main suspension cables, atmospheric corrosion, accelerated corrosion testing, pitting, eutectoid steel, acid rain

Background

The Williamsburg Bridge spans the East River in New York City, connecting the boroughs of Manhattan and Brooklyn. The main span of the bridge opened in 1903, is some 488-m long, and carries both automobile and rail traffic. The roadway is suspended from four main support steel wire cable bundles that pass over tower columns 91-m high and are embedded in concrete anchorages.

An extensive inspection/rehabilitation program for the Williamsburg Bridge has been conducted over the past several years. This program has revealed corrosion and pitting damage to the cable wires. In some cases these pits occupy one-third of the diameter of the cable. Once it was established that the cables had suffered atmospheric corrosion damage, it became necessary to decide if the cables could be rehabilitated, or if replacement was necessary.

The key to determining if the cables could be rehabilitated was to assess the degree of damage that the wires in the cables have suffered and the extent to which additional damage will occur in the future. These assessments could be made only if the physical mechanism(s) controlling the corrosion damage could be determined as well as the past, present, and future rates at which

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this corrosion damage proceeds. Such information, in addition to permitting an estimate of the future life of the cables, would assist in the development of possible remedies to alleviate the progression of corrosion-based damage.

The objectives of this research were to assess and quantify the chemical and physical mechanisms operating on the cables, to determine the rate at which these mechanisms are progressing, and to use this information to estimate the rate at which this damage will progress in the future. In the balance of this section, some of the design, construction, and environmental factors contributing to the corrosion mechanisms are discussed.

Cable Construction and Load

The safety and existence of a suspension bridge depends entirely on the strength and integrity of its cables. On the Williamsburg Bridge, each of the four cables contains 7696 No. 6 gauge (4.88-mm-diameter) bright steel wires. The cables are approximately 852 m long, which means there are over 26,200 km of wire in these cables.

Because of the increase in traffic, the increase in the weight of the vehicles, and various modifications that were made to the bridge since it was built, the load supported by each of the four main cables has increased. The tensile force in each cable initially was estimated to be 48,100 kN, which has now increased to 54,500 kN [1]. This force is the sum of the live load caused by traffic, the static load caused by the weight of the bridge itself, and the wind loading. Approximately 75% of the total load on the Williamsburg Bridge cables is caused by the static weight load. Based on the current maximum force in the cable (54,500 kN), and assuming there are no broken wires in the cable and that corrosion has not reduced the wire diameters at any point along their length, the force each wire currently supports is 7.08 kN. This corresponds to a tensile stress of 379 MPa on the cable or the individual wires (if the load is equally distributed among all wires).

Bridge Environment

The bridge itself is located in the middle of a major urban industrial region and is thus exposed regularly to aggressive atmospheric pollutants like sulfates, which are commonly found in highly developed areas [2]. In addition, the bridge is within a few miles of the Atlantic Ocean and is thus exposed to marine air and fogs containing salts. The East River is brackish at the location of the bridge. The weather in New York is often below freezing in the winter, requiring the use of salts to de-ice the bridge deck.

The mean monthly relative humidity year-round in New York City is always greater than 70% [3] based on twenty-year averages beginning before 1960. The time of wetness is a complex function of relative humidity, surface contaminants, and surface roughness; however, when it rains the cable and the wires inside the cable in general will be wet or damp. The mean annual number of days in New York City with precipitation exceeding 0.254-mm is 135 [3] based on data collected from 1931 to 1960. The mean annual pan evaporation for New York City is 813 to 1222 mm, which is low compared with most of the rest of the country [3]. The mean annual pan evaporation is a measure of how rapidly water and moisture will evaporate from a surface and is controlled by temperature, sunshine, and relative humidity. From these data, we can estimate that the bridge wires will be damp at least 135 days of the year and perhaps even longer because of the relatively low evaporation rate for exposed surfaces.

In addition to the effects of humidity and rain, the time of wetness and corrosion are affected by the presence of atmospheric pollutants. These pollutants can affect time of wetness by introducing hygroscopic corrosion products to the metal surface [4]. In addition, these pollutants introduce reactive ions and affect the pH of solutions the metal is exposed to, which greatly affects the rate and type of corrosion.

Atmospheric pollutants that have an effect on the corrosion of metals have been identified as sulfur dioxide (SO₂), nitrous oxides (NO_x), ammonia (NH₃), and particulate matter [5]. Atmospheric sulfur and nitrogen oxides are emitted from both natural and anthropogenic sources [6]. The largest sources of these oxides in the New York City area are anthropogenic. These oxides will hydrolize and further oxidize in the atmosphere and yield sulfuric acid (H_2SO_4) and nitric acid (HNO_3) [7]. The result is acid precipitation. New York City is in one of the regions with the most concentrated (lowest pH) acid rains in the United States. This acid rain condition, combined with road deicing salts, humidity, and marine environments, result in a severe atmospheric corrosion environment for the Williamsburg Bridge.

Cable and Cable Wire Coatings for Corrosion Protection

When the New East River Bridge (now known as the Williamsburg Bridge) was being planned, the Brooklyn Bridge cables were 24 years old and inspection found them free of corrosion. It was not known if this was caused by the use of galvanization or whether the same results might have been obtained without galvanization [8]. Therefore, it was decided to use a new (and, hopefully, improved) method for protecting the cables by enclosing them with a waterproof covering. Bright, ungalvanized wire was selected for the bridge wire because this wire was stronger than galvanized wire and fewer wires could be used to make each of the four cables. Galvanized wire is generally weaker than bright wire because of the annealing that takes place during the hot dipping process. This annealing heats the wire to 427° to $482^{\circ}C$ and results in a strength loss of about 3%.

The cable specification called for the bright wire to be given two coats of linseed oil. After the wires were banded into strands during the spinning process, they were to be thoroughly covered with a compound known as Cable Shield. This compound was to fill all the spaces between wires in the strands and the space between strands. The finished cable was then to be coated with Cable Shield. The cable was tied together at only a few locations with the helical wire wrappings. The cable was then to be enclosed in a sheet-iron covering to make the cable absolutely waterproof.

Problems arose, however, when it was found that Cable Shield was too viscous to permit it to be satisfactorily applied to the cables. This proprietary compound of pine tar and other ingredients penetrated only the first or second layer of wires in the cable. As a result, slushing oil was used instead of Cable Shield.

The slushing oil, a petroleum-based product, was mixed with 25% artificial graphite. The graphite served as a lubricant to make it easier to compact the wires in the cable and to increase the viscosity of the slushing oil. To ensure that each wire would be coated with at least one coat of slushing oil and graphite, the original plan for coating the wire with two coats of linseed oil was changed to one coat of linseed oil and one coat of slushing oil with graphite. It was hoped that the coating of slushing oil would remain pliable, but it was found that on exposure to the New York atmosphere for five or six months, the coating dried and became defective in places and required frequent retouching.

There was concern that although the outer sheet-iron covering around the cable might be waterproof, it would not be airtight, and this would cause the moisture in the entrapped air to condense and precipitate in the cable. This condensed water would then be trapped within the cable. For this reason, it was decided to have the slushing-oil-covered cable enclosed with a waterproof wrapping. The cable was thus wrapped with three layers of a waterproofed cotton duck. The cable plates, made from 1.59-mm-thick sheet iron, were then placed over the cotton duck. The joints between the cable bands and the cover plate, and the seam between the upper and lower halves of the cover plates were then coated with an oxidized linseed oil coating.

Cable Inspection and Maintenance History

Despite these attempts of the cable designers, the Williamsburg Bridge cables have had a history of recorded corrosion problems. As early as 1910, only seven years after the bridge was opened, the cable had experienced corrosion damage and broken wires were found. The reports on the maintenance and inspection procedures in the early years do not seem to be complete; however, there were 14 known broken wires found in the anchorage in 1910. In 1912, rust was found to have developed in the cable at the center of the span, and some wire samples were taken at that time for analysis. The disposition of this wire is not known. As a consequence of this discovery, funds were provided for removing the outer sheet metal cladding and canvas wrapping. The cable was coated with oil and rewrapped with galvanized No. 8 wire. This work was done between 1915 and 1922.

In 1934, water was found to run out of the cable strands in the anchorages, and areas of severe rusting were found on the strands. Reports, which may be incomplete, list 320 broken or seriously corroded wires in the Brooklyn anchorage. These wires were replaced by splicing in new galvanized wire between 1934 and 1935.

Given this problem-plagued history, the Williamsburg Bridge cables were subjected to an extensive inspection and rehabilitation program between 1980 and 1985. Some of the experiments and analyses obtained as part of this program are discussed in the balance of this paper.

Experimental Methods

Cable Wire Sampling and Characterization

The size, loading, and inaccessability of the cables precluded any form of nondestructive inspection technique, such as x-ray or eddy current, from being used to characterize the extent of corrosion damage. As a result, the direct physical inspection method was chosen. In 1982, the American Bridge Division of United States Steel Corporation unwrapped a 91-m segment of Cable B from the Manhattan-side back span region and pulled approximately eighteen 91-m lengths of wire at different clock positions (see Fig. 1). New wires were spliced back in to replace the pulled wires. Because of difficulties in penetrating the wire bundle, only wires within the top 6-cm of the cable were pulled. These pulled wires provided the specimen material for the detailed physical and mechanical examinations conducted both by United States Steel Corporation and by SRI International.

This 1638-m sample of cable wire represents only a very small fraction of the total length of wire in the four cables (some 0.006%), and only strictly represents the condition of the wires near the surface of a cable. Nonetheless, it was the best sample that could be obtained given the physical limitations of the bridge. Obviously, it is impossible to check how well this sample actually represents the condition of all wire in the cables without actually dismantling the cables. However, the location on the cable from which this sampling was taken did not represent the most heavily damaged regions.² Therefore, any extrapolations of the results of actual cable wire conditions.

To determine if the wires contain subcritical stress corrosion cracks, we first selected at random several segments (totaling 5.5 m) of the pulled wires. Segments of heavily corroded wires, lightly corroded wires with in-situ breaks, and wires pulled to failure in the 57-m tests were selected. Each segment was cut into 127-mm lengths and mounted in epoxy. The wires were

²For instance, detailed visual inspections suggest that the damage to wires in the splay region of the anchorage is more severe than the damage to wires in the back span region. Unfortunately, it proved to be too difficult to obtain long wire samples from the splay region.



FIG. 1-Schematic cross section of main cable.

then carefully ground until approximately half of the diameter remained. Finally, these "longitudinally sectioned" wires were metallographically polished and examined with optical microscopy.

The chemistry of the wire and associated corrosion products were determined by spectrographic and wet chemical analysis. Some broken wires were found when the cable was unwrapped and these in-situ fractures and the fracture surfaces from the short and long gage tensile tests were examined by scanning electron microscopy.

Mechanical Properties

Since 1980, three types of mechanical tests have been performed on samples of bridge wire removed from the cables to ascertain their load bearing capacity: the 25.4-mm smooth gage length tensile tests that SRS performed, the 254-mm as-corroded gage length specimens tested in tension and fatigue by U.S. Steel, and 57-m as corroded gage length specimens tested by U.S. Steel.

The 25.4-mm smooth gage length specimens were used to help estimate the initial strength of the bridge wire when all the surface defects have been removed. The 254-mm and 57-m ascorroded gage length specimens were used to estimate the current breaking load of unbroken wires in the cable. This breaking load was expected to be lower than that calculated based on the initial strength and wire diameter caused by corrosion induced surface defects. The 25.4 and 254-mm tensile tests were performed on standard tensile test machines at engineering strain rates of about 10^{-3} s⁻¹. The 57-m gage length tensile tests were done on a specially constructed draw bench.

Accelerated Corrosion Testing

To simulate the corrosion of bridge wires, we developed a test method to reproduce many of the features of the cable environment. This test exposes wires that are in the center of a 50.8mm-diameter wire bundle to the test solution for 15 min; the specimen was then removed from the solution to dry for six h, and the cycle was repeated. The cycling was done in an enclosed chamber to keep out dust and maintain a relatively high humidity. This apparatus is shown in Fig. 2. The temperature and relative humidity within this chamber was continuously recorded. During each cycle there was both a temperature and relative humidity fluctuation, but the temperature averaged 18.3°C, and the relative humidity varied only between 50 and 65%. It took about five h for the test wire at the center of the wire bundle to dry out. This means that during most of the test cycle, the relative humidity at the test wire was 100%.

The bundles of wires are shown in Fig. 3. The wire bundles were made up of approximately 22 wires cut from the bridge wire. We measured the corrosion rate on the center wire of each bundle. These wires were cut from wire that was in "good" condition (little apparent corrosion) and from wire that was in "bad" condition (clearly corroding). The cut ends of the wires were epoxied, and the exposed surface area was measured. The wires were carefully weighed and placed in the center of the 50.8-mm-diameter wire bundle. The bundle was held tightly together with stainless steel hose clamps, which were carefully insulated from the wires by means of Teflon sheet to prevent any galvanized couple.

To determine what water chemistry the wires were exposed to, we analysed about a gallon of water that had been collected at the bridge site during a rain storm. The chemical analysis of this water is shown in Table 1, along with an analysis of "synthetic rainwater" we made up to use in our accelerated corrosion tests. Note from Table 1 that this synthetic rain water closely simulates the chemistry of water that had been collected from one of the cables on the bridge. The pH of both solutions is about 4.3, and the SO_4^{2-} and CI^- concentrations of both solutions closely match. Nitrates were not included in the synthetic solution for reasons discussed in the results section.

Three separate dip tanks were established for the accelerated corrosion tests. For base line data, deionized water was used in one of the dip tanks. The other two tanks used the synthetic acid rain. The deionized and synthetic acid rain solutions were constantly aerated during the testing. The test solutions were replaced, during a drying cycle, once a week.

The effect of a vapor phase inhibitor on the corrosion of bridge wires was evaluated in synthetic acid rain in a third tank. The separate tank was used to prevent the inhibitor from washing off an inhibited sample and depositing on an uninhibited specimen and confusing the test results. The inhibitor was a commercially available vapor phase inhibitor known as CORTEC[®] VCI-369. This inhibitor was diluted with mineral spirits with a 1:1 volume dilution in accor-



FIG. 2-Accelerated corrosion test facility.



FIG. 3-Typical wire bundles for each environment from accelerated corrosion tests.

	or ppm.	
Species	Bridge Water	Synthetic "Acid Rain"
NH ₃	1.9	3.0
HCO ₃	5.5	6.0
Ca	4.0	4.0
Cl	7.3	8.1
Na	6.0	6.0
SO₄	8.0	6.0
Zn	0.5	0.11
NO ₃	1.7	
pH⁴	4.3	4.3

TABLE 1—Chemistry of synthetic acid rain,	mg/L
or ppm.	

"pH of pure water saturated with CO₂ is 5.6. "Acid rain" is defined to be rainwater with a pH < 5.0.

dance with the manufacturer's specifications. The wire bundles were immersed in this solution; penetration by this inhibitor was such that all wires were coated using this method. Excess solution was drained off and the inhibited bundles were placed in the test rack.

The amount of corrosion product on the center wire of a wire bundle exposed to a given number of wetting/drying cycles was measured by the mass loss method. The center wire was weighed and then placed in Clarke's solution. This solution removed some of the corrosion product and the wire was reweighed. This procedure was repeated until the mass loss rate became linear with time, indicating that all the corrosion products have been removed. The linear region was extrapolated back to zero cleaning time to obtain the corrosion product mass loss. The wire was then discarded (acid cleaned wires were not reused). This wire cleaning operation gave one point on the curve of mass loss versus cycle number, and was repeated for each mass loss/cycle number data point.

Results and Discussion

Visual Inspection Results

The wires pulled by American Bridge and inspected by SRI are identified in Fig. 1. At least one wire was pulled from the outside of the bundle at each of the twelve o'clock positions. In addition, several wires were pulled from the twelve and six o'clock positions some six cm into the bundle and were identified as wires 13, 14, and 15. Several wires were pulled from the six o'clock position, but broke into several segments during removal.

By and large, the bulk of the corrosion damage on all the pulled wires was in the form of pits, or localized corrosion. These pits ranged in depth and diameter from tens of micrometers to one-third of the diameter of the wire. As with earlier inspections, many of these pits were obscured by the slushing oil compound. As indicated in Fig. 1, the size and number of pits on the wires gradually increased toward the six o'clock position. The most severely damaged of the identified wires were the ones pulled from the six o'clock position. The worst damage, however, was observed on some of the unidentified broken wire segments, which available evidence indicates were also removed from the six o'clock position. It thus appears that the worst pitting corrosion damage occurs at the bottom of the cable and that this damage extends unabated at least several centimeters into the cable bundle.

Figure 4 illustrates the range of damage found on the wires. Some of the wires, particularly those found near the twelve o'clock position, were in very good condition. Few pits were readily visible on the surface of the wire. Removing the slushing oil coating from these wires uncovered few additional pits. After cleaning, these good wires exhibited the shiny appearance of new "bright" wires. Wires removed from the six o'clock position, however, generally exhibited a mottled, rough surface appearance. Removal of the slushing oil from these bad condition wires revealed numerous large and small pits all along the length of the wires. There was no preferential attack on one side of the wire relative to the other sides.

The type of corrosion observed on the bridge wires appears to be pitting corrosion. This pitting can be attributed to the following factors:

• The wire had only one protective coat of linseed oil. The graphite and slushing oil coating applied over this was probably not very protective. At any rate, when the cable was being "spun," the wires were damaged in spots. These damaged areas were repaired, when noticed, with slushing oil and graphite; however, there were undoubtedly areas that were missed. In addition, over the years many additional areas were probably damaged by wires rubbing against one another as a result of the wind loading on the cable. These bare spots on the cable are now undergoing localized corrosion.

• The bare areas that are now exposed to the chloride-containing acidic bridge environment will not form a protective corrosion product. The chloride will prevent this by attacking the protective oxide in certain areas in which it forms. The combination of pH, electrochemical potential, and chloride ion concentration to which the wire in the cable is exposed puts the wire right in the proper region of the potential/pH diagram to cause pitting, as shown in Fig. 5 [9,10]. The electrochemical potential of the bridge wires is controlled by the amount of oxygen in the rainwater solutions. The pH dependence of the electrochemical potential is given by line b in Fig. 5. If no oxygen were present in solution, the potential would follow line a. For a solution of pH 4.3 and a potential that lies anywhere from the oxygen-saturated line to the no-oxygen line, we can see that the corrosion will take the form of pitting.



FIG. 4-General appearance of surface of wires removed from bridge cable.



FIG. 5-Influence of chloride on the pitting tendencies of iron.

• The regions of bare metal will also be in contact with regions coated with slushing oil and graphite. The graphite in this coating is conductive; furthermore, it can form a galvanic couple with the bare metal. The potential difference between the steel and the graphite can be as high as 1.0 V [11]. The graphite will act as the cathode, which will have an enormous surface area compared with the surface area of the bare metal. The corrosion rate in this small bare metal area must be high enough to support the cathodic reaction occurring over a much larger graphite-containing area. Thus the growth rate of the pits into the wire will be much higher than if the anodic and cathodic regions were of equal area and microscopically distributed over the surface.

• Rainwater and moisture can diffuse into the linseed oil coating along with aggressive ions such as chloride and sulfate. The solutions that diffuse through the coatings will attack the metal at areas where inclusions intersect the surface and where graphite particles in the coating are in contact with the metal. This attack will occur at the graphite particles because of the galvanic couple and the differential aeration cell that is set up at the interface between the graphite and steel.

Optical microscopy of the 5.5 m of sectioned and polished bridge wires yielded no definite indications of stress corrosion cracking (SCC). Nonetheless, we do not believe this cracking process can be ruled out in the future. Steels are known to be susceptible to SCC in environments containing nitrates and hydroxides. In addition, high strength steels with yield strengths greater than 1240 MPa are known to crack in both pure and impure water [12]. The yield strength of this bridge wire is well above these levels and some NH₄NO₃ and NaNO₃ are present in the rainwater (see Table 1) as well as other potential SCC-causing constituents. Recall that the New York City area is in one of the highest NO_x areas of the United States [3]. Furthermore, the bridge wire is in a cold-drawn and tempered condition, and bridge wire steel in the cold drawn and stress relieved condition is considered to be more susceptible to hydrogen or stress corrosion cracking than cold drawn steels [12]. These factors all suggest that SCC ultimately could become the dominant failure mechanism for the bridge wires.

In conclusion, visual inspections of the 254-mm and 91-m segments showed that the principal corrosion mechanism was pitting, but no correlation could be made between the location of the pits on an individual wire and surface defects or flaws in the slushing oil coating. The size, depth, and number of pits on wires removed from the outside surface of the cable generally increased from the top of the cable to the bottom. The worst damage was observed on wires pulled from the six o'clock position several centimeters deep into the cable bundle. On the heavily corroded wire, there was a broad distribution in pit size, depth, and number, with some of the pits penetrating up to 30% of the wire diameter. Most pits found on all wires examined, however, were less than $610 \mu m$ deep. For the most part, the pitting damage was evenly distributed around the circumference of a wire.

Chemistry and Microstructure Results

In 1980, samples of wires taken from cable D were submitted for quantitative chemical analysis by U.S. Steel. The results of this analysis are given in Table 2, along with typical compositions of more recent bridge wire. It is apparent that the composition of the Williamsburg Bridge wire is very similar to that of modern wire. The low P, S, and other residuals indicate that care was taken in selecting the materials that went into making this wire and in melting and casting the steel. Steel produced in the late 1800s, made without the benefit of modern foundry practices, often had a very high impurity content. Thus this steel is unusually "clean" for this era.

		Typical Wire	Used in 1940s
Element	Williamsburg Bridge	Portsmouth Bridge ^a	Mt. Hope Bridge
C	0.82	0.83	0.7 to 0.8
Mn	0.44	0.53	0.4 to 0.6
Si	0.03	0.14	0.12 to 0.20
Р	0.028	0.008	0.04 max
S	0.018	0.029	0.04 max
Fe	balance	balance	balance
Cu	0.05	NA	NA
Ni	0.01	NA	NA
Cr	0.01	NA	NA
Mo	0.005	NA	NA
Sn	0.003	NA	NA
Al	0.03	NA	NA

TABLE 2—Chemical composition of cable wire, wt%.

"Data taken from Ref 14.

Mechanical Property Results

A key piece of information required to properly assess the degree of damage to the cables was the initial (uncorroded) strength of the individual wires. A survey of the construction documents on the bridge suggested an ultimate tensile strength of about 1550 MPa, but this could not be confirmed. Also, because several different lots of wire were used, it was important to determine and quantify the statistical distribution of wire strengths.

The smooth, 25.4-mm gage length experiments performed by SRI showed that the mean breaking force of uncorroded wire was 29.2 ± 1.69 kN (167 observations). The mean total elongation to failure was determined to be $6.4\% \pm 2.1\%$ (153 observations). We believe that the mechanical properties data we determined from the tests on 25.4-mm gage length wires with all surface defects removed accurately reflect the original mechanical properties of the wires in the cable. The variances in the mechanical properties data on the wires free of surface defects reflect primarily the variation in the thermomechanical processing history and chemistry of the different lots of wires that make up the cable.

In 1982, U.S. Steel Corporation conducted 57-m gage length tensile tests on the 91-m lengths of wire pulled from the cable with the as-corroded surface condition. These tests showed that the current average breaking force of approximately 57-m lengths of wire appears to be about 25.6 kN, or about 3.6 kN lower than when the wire was originally installed. Examination of the fracture surfaces with scanning electron microscopy showed that this apparent loss of breaking strength is caused by pitting corrosion damage to the wire surfaces. This corrosion reduces the load-bearing area of the wire and therefore its load-bearing capacity. Examination of the surfaces of wires found broken in the cable also showed that these fractures were initiated at corrosion pits.

Other tensile tests on corroded wires of different gage lengths [14] clearly showed a trend of decreasing breaking load with increasing gage length. This effect is explained by the increased probability of finding a deeper pit as the gage length is increased. The only other explanation is that the probability of finding larger inclusions should increase as the length increases; however, this hypothesis is not compatible with the fractography and metallography of the tested wire, in that the fracture surfaces in general did not appear to have a higher density or a larger size inclusion as the test length was increased. Rather, the fractures were associated primarily with pitting for both the in-situ and the laboratory-induced fractures. Specifically, the reduc-

tion in breaking strength observed in the 57-m tests is a result of these pits which ranged in depth from 152 to 610 micrometers.

Accelerated Corrosion Test Results

The chemical analysis of the rain water from the bridge reported in Table 1 indicates that the New York rainwater is indeed acidic. The pH of pure water that is air-saturated is about 5.6 because of the CO_2 absorbed from the air. Acid rain is not well defined, but rainwater with a pH of less than 5.0 would most certainly be considered acidic. The value we measured in the rain water was 4.3.

The bridge wire water contained sulfate (SO_4^{-2}) and (NO_3^{-1}) ions from the sulfur and nitrogen oxide atmospheric pollutants. These constituents were primarily responsible for the low pH. The low pH in conjunction with the chloride ions was primarily responsible for the pitting of steel and was reproduced in the synthetic rain water test solution. The New York City area has nearly the highest SO₂ concentration $(83 \ \mu g/m^3)$ [15] in the Northeast. These SO₂ values, collected over the period 1961 to 1965, have been declining slowly in recent years because of pollution control efforts, but were included in the synthetic solution for completeness. Nitrates, on the other hand, have been implicated in stress corrosion cracks of bridge wires, [12] but do not enhance pitting or localized corrosion of steels [13]. Since the accelerated corrosion tests were designed to simulate pitting (the observed corrosion mechanism) and not cracking, nitrates were omitted from the synthetic acid rain test solution.

The relatively high chloride ion concentration in this water probably comes from two sources. The first is the use of deicing salts [calcium chloride (CaCl₂) or sodium chloride (NaCl) or mixtures of both] used on the bridge in the winter. The melted snow/salt solution is then atomized by the traffic, and some of these salt solution droplets deposit on the cables. The salt eventually finds its way into the cable. The second source of chloride is the bridge's proximity to the ocean and the brackishness of the East River. It is well established that chlorides can contribute to the pitting of steels, and therefore were included in the synthetic test solutions.

The other chemical species reported in Table 1 are not significantly involved in the uniform or pitting corrosion process. The zinc ions result from the zinc metal present in the paint on the exterior of the helical wound wire cable wrap. All these "inert" species were included in the synthetic test solutions for completeness.

The results of the accelerated corrosion tests shown in Fig. 6 indicate that the corrosion seems to be proceeding at a linear rate with number of cycles. These plots also clearly indicate that the inhibitor slows the corrosion rate. In the synthetic acid rain water, both good and bad wires seem to corrode at about the same rate, whereas in deionized water, the good wires corrode at a significantly lower rate than wires in the bad condition. We interpret this to mean that the acid rain causes good wire to start corroding or pitting immediately at a rapid rate, whereas the good wire exposed to deionized water corrodes at a much lower rate.

The corrosion rate of bad wire exposed to deionized water is about the same as that noted for corrosion of good or bad wire exposed to synthetic acid rainwater. This behavior seem to indicate that, once the corrosion products and pits develop on a wire, they continue to corrode rapidly even in a less aggressive environment. This can be explained by either the autocatalytic nature of pitting or the trapping of contaminants in the corrosion products from the real environment and the contaminants being carried over to the deionized test solutions.

The mean, upper, and lower bounds on the rate of metal penetration per cycle are reported in Table 3. The upper and lower bounds represent the 95% confidence interval for the slope of the metal penetration versus cycle data. The mass loss was converted to the penetration data, shown in Table 3, by assuming that the corrosion was taking place uniformly around the circumference of the wire and using standard ASTM procedures.

The information we want, however, is not the amount of metal penetration per cycle but the



FIG. 6-Corrosion rates from accelerated corrosion tests.

Water Type	Wire Condition	Inhibitor	Slope Mean	(nm/cycle) Upperª	Lower"	Mean	Intercept, μm Upper ^a	Lower"
Rainwater	good	no	39.9	45.5	34.3	2.80	3.66	1.91
Rainwater	bad	no	31.5	87.1	0	16.0	24.8	7.22
Deionized	good	no	0	12.2	0	2.52	4.53	0.712
Deionized	bad	no	45.5	71.9	19.1	6.38	10.5	2.19
Rainwater	good	ves	0	6,48	0	1.50	2.62	0.381
Rainwater	bad	yes	11.9	17.9	5.99	4.48	5.42	0.356

TABLE 3-Corrosion rate from accelerated corrosion tests (all data from 6 O'clock wire).

"The upper and lower limits represent the 95% confidence interval for the intercept and slope of the regression equation.

amount of metal penetration per year of exposure to actual cable environment. To convert the data in Table 3 to the actual metal penetration the cable wires are undergoing *in situ*, we need two additional pieces of information: (a) the amount of actual area corroding and (b) how many of our wetting/drying cycles correspond to a year of exposure in the cable.

The first piece of information can be estimated from the results of our examination of the corroded bridge wire. Visual examination of the wires showed that the area fraction corroded by

pitting varies from about 30 to 70%. The remainder of the wire is corroding uniformly. Based on this observation, we used an area fraction of 50% to estimate the actual pit propagation rate.

The number of cycles per year of exposure is more difficult to estimate. The relative humidity of New York City is always fairly high and once water or condensate is present in the cable it takes a long time to dry out because of the hygroscopic corrosion products present in the cable. Thus a reasonable assumption would be that one cycle corresponds to one day of exposure. We feel that this is the upper limit based on some research that has been done on accelerated atmospheric corrosion tests on copper alloys using a wet/dry cycle similar to the one we have used [14]. In this work, each wet/dry cycle was equivalent to about one day of outdoor exposure in New York City. This factor was based on the comparable appearance of specimens exposed for several years in New York City and specimens exposed for short times to accelerated tests. A lower limit can be estimated by assuming that one cycle is equivalent to one rainy day. There are on the average 135 rainy days per year in New York City as discussed previously. From these estimates of cycles/year and area fraction corroding, the metal penetration rate can be calculated for uniform and pitting corrosion. The mean and 95% upper limit for these types of corrosion rates are reported in Table 4.

In conclusion, our accelerated corrosion experiments on bundled and single bridge wire specimens indicate that the current localized and pitting corrosion rates lie somewhere between 15.2 and 63.5 μ m/year of metal penetration. Furthermore, our preliminary experiments with a vapor phase inhibitor (VCI-369) suggest that it can substantially reduce this corrosion rate in a laboratory environment if properly applied. However, because of the uncertain nature of the current extent of corrosion damage done to the cable wires, the questions regarding the permeability of the vapor phase inhibitors, and the possible enhancement of SCC if inhibitors are applied at low concentrations, the use of these inhibitors as a cable rehabilitation method cannot be recommended.

Corrosion Damage Model

Because there is no easy way to determine the distribution and extent of the corrosion damage to the cable with any great accuracy, a computer model [15] was developed to estimate this damage. The model uses as input the initial and current (1982) strength of the wires, the expected pit growth rate, and an estimation of the amount of frictional load transfer between broken and unbroken wires in the cable. The output is the pit initiation rate, the breaking strength of the wires, and the number of broken wires in the cable. This allows the calculation of the cable strength at any point in time. The details of this model will be the subject of a separate paper, but the key predictions are as follows. Using a pit growth rate of 25.4 μ m/year (which is based on our laboratory experiments) and an effective frictional clamping distance of 122 m, the model predicts that the safety factor has been reduced from four to about 2.5, and is rapidly decreasing (Fig. 7). This model is not considered to give an accurate absolute prediction of the

Parameters 135 Cycles/Year	365 Cycles/Year
Percent of corroding area, % 50	50
Mean corrosion rate	
slope, nm/cycle 39.9	39.9
average general corrosion rate, $\mu m/year$ 5.38	14.5
average pit propagation rate, $\mu m/year$ 10.8	29.2
Maximum corrosion rate	
slope, nm/cvcle 87.1	87.1
maximum general corrosion rate, $\mu m/vear$ 11.8	31.8
maximum pit propagation rate, μ m/year 23.5	63.5

TABLE 4—Mean and maximum corrosion rates estimated from accelerated corrosion tests.



FIG. 7-Pitting corrosion computer model prediction for residual life of cables.

cable strength, although it seems to be in reasonable agreement with all known observations, including a large scale static load test and finite element analysis of the bridge.

The utility of the model is its ability to describe how the load bearing capacity of the cable is affected by changes in the corrosion rate, frictional load transfer, and initial wire strength. For instance, Fig. 7 shows the effect of inhibitor addition in extending the life of the cables. In this case, it was assumed the inhibitor was added in 1983. The effect of the inhibitor is illustrated by assuming it reduces the pit growth and initiation rates in several ways. This shows that inhibitor application could increase cable life if properly applied. However, for the reasons previously discussed, it is not considered a reliable rehabilitation method.

Conclusions

Based on our work with samples taken from the main suspension cables of the Williamsburg Bridge, we can draw the following conclusions:

1. The physical mechanism of damage to the cable wires was confirmed to be pitting and localized corrosion; however, hydrogen-induced stress corrosion cracking of the wires cannot be ruled out.

2. The current ultimate breaking force of uncorroded wires was determined to be 29.2 \pm 1.69 kN, which we believe accurately represents the original strength of wire. The average breaking force of a group of corroded and uncorroded wires in the cable was determined to be 25.6 \pm 3.69 kN, indicating that corrosion processes have reduced the load-bearing capacity of the bridge wires.

3. The rate of localized and pitting corrosion was estimated to be between 15.2 and 63.5 μ m/ year metal penetration.

4. For a corrosion rate of 25 μ m/year (which we believe represents a realistic value), our strength degradation model estimates that the present safety factor of the cable is 2.5 and that it will drop to 1.7 by 2005 by summing the breaking forces of uncorroded wires and corroded but unbroken wires. This estimate also assumes that once a wire is broken, it can still carry the load it was initially bearing at distances greater than 122 m from the break caused by frictional load transfer.

Acknowledgments

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DISCUSSION

B. Isecke¹ (discussion question)—What were the results in fracture appearance in the SEM inspection? Was there any difference in the initial fracture zone and the fracture preparation area? What was the actual mechanical loading of the steels? In my opinion the fractures occurred as a result of the interaction between corrosion environment and mechanical loading. The fracture initiation is given by the local pitting. The propagation of the fracture is resulting from anodic solution of iron in the crack tip and increasing mechanical loading the crack which lead to local stresses higher than the yield strength. The evolution of hydrogen at the crack tip could also be an important factor as in areas where the access of oxygen is limited to pH de-

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creases and as a cathodic reaction in the corrosion process hydrogen can be evolved. This may not play an important role in this case if the mechanical stress in service was very much below the yield point.

L. Eiselstein (author's closure)—In answer to the first and second questions about the appearance of the fracture surfaces of wires found broken in the cable, as part of our program we examined six in-situ fracture surfaces. These fractures were, in general, extremely corroded. The corrosion product on the fracture surfaces were carefully removed by electrochemical cleaning. Figure 8 shows a SEM fractograph of one of the in-situ failures. The in-situ fractures were found to have initiated at shallow-broad surface pits. Due to the long time the fracture surfaces were exposed to the environment, most of the features of the initiation zone were obliterated. However, regions close to the base of the shallow-broad surface pits showed signs of ductile



FIG. 8—Fracture surface of wire segment A-1, which failed in-situ in the cable splay region of an unidentified anchorage.

microvoid coalescence. The propagation zone of the fracture surface was definitely ductile failure. The general features of the in-situ fractures are consistent with a failure scenario in which the cross-section of the wire was reduced by localized corrosion or pitting to a level at which the applied load on the wire exceeded the ultimate tensile strength of the bridge wire.

In answer to the third question the actual mechanical loading of the wire in the cable comes primarily from the static load of the bridge. This results in an average tensile load on the wire of 373 MPa (assuming the cable contains no broken wires).

Most of Dr. Isecke's questions and his remarks seem to be directed at whether or not SCC or hydrogen embrittlement (HE) was a factor in the bridge wire failure mechanism. This question was a major concern since SCC and HE is a much more serious problem for the bridge wire than pitting corrosion since the crack growth rates can be much greater than pit propagation rates. The detailed fractographic work on wires found broken in-situ or pulled to failure in laboratory tensile tests did not conclusively show that SCC or HE had or was occurring. To determine if subcritical SCC or HE cracks were present in the cable wire, randomly selected segments of wire (totaling 5.5 m) and short segments containing in-situ fractures were longitudinally sectioned, metallographically polished and examined with an optical microscope at $100 \times$.

We were unable to detect any evidence of SCC or HE cracking in the 5.5 m of wire that we sectioned and polished. Nonetheless, time-dependent, environmentally induced crack growth from surface pits cannot be entirely ruled out. For example, hydrogen-associated stress corrosion crack growth can exhibit fracture surface topologies similar to those shown in Figure 8 (i.e., enhanced microvoid coalescence). In this process, the cracks would tend to initiate at the bottom of only the deepest pits. Then, by a time-dependent hydrogen-diffusion-controlled mechanism, these cracks will propagate across the diameter of the wire until an overload condition is reached. In this case, one can argue that the amount of secondary cracking associated with this process would be minimal. Therefore, it is possible that some of the in-situ fractures we examined were caused by hydrogen-assisted stress corrosion cracking. Furthermore, 5.5 m represents less than 0.00003% of the total length of wire in the cable. As a result, although hydrogen-assisted stress corrosion cracking is not apparent, we cannot prove that it has not occurred somewhere within the cables. Also, even if stress corrosion cracking has not yet occurred, if the currently operative general corrosion and pitting processes are allowed to continue unhindered, the rate of stress corrosion cracking will almost certainly increase sometime in the near future.

Observations on Atmospheric Corrosion Made of Architectural Copper Work at Yale University

REFERENCE: Fishman, H. B., Darling, B. P., and Wooten, J. R., "Observations on Atmospheric Corrosion Made of Architectural Copper Work at Yale University," Degradation of Metals in the Atmosphere. ASTM STP 965. S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, p. 96-114.

ABSTRACT: A six-year study of roofing and flashing of various buildings including many at Yale University was conducted. The buildings had architectural copper, which was in service for up to 100 years or more. There was great variety of usages. Various components had failed while others were salvageable and still others only slightly worn. Because of the varying degree of wear we attempted to find the reasons for this degradation. Methods of installation, location, orientation, and other factors were evaluated. Samples were taken, measured, and photographed. Some samples surfaced with lead faired better than some with no coatings. Lead coated copper on vertical surfaces did not wear as rapidly as on flat surfaces. Contaminants in the atmosphere appeared to increase rates of corrosion. Asphaltic or aluminum bearing repair materials produced adverse affects and were ineffective in stopping the leaks. Lead coating and patina were important in reducing the rate of aging. Size and method of restraint were also important. Large panels were subject to fatigue and cracking. Pitting at soldered seams was frequently observed. Photographs depict various sequences. Formation of patinas in corrosion products were observed. Lead coated copper was found to turn green after approximately 25 to 35 years of exposure on horizontal surfaces. Vertical surfaces remained grey or white. Reduction of serviceability depended more on method of installation, detailing, and design, than on the corrosion-induced deterioration.

KEY WORDS: atmospheric corrosion, copper roofing, fatigue, Yale, copper flashing, patina

Copper roofing sheets have been used for hundreds of years. Studies on atmospheric corrosion usually center on highly technical calculations and observations of the actual atmosphere. This study, however, centers on visual observation and measurements of samples taken directly from buildings whose metal work was being studied to determine whether the roofing should be repaired or replaced. Inspections were made prior to the start of construction, and data thus gathered was employed in the design of the new work. New work was observed during the construction term. Photographs and samples were taken. The age of the copper was estimated according to the age of the building. In some cases in which copper was repaired or replaced previously, adjustments were made. The years of exposure of the various sheets were estimated and are not necessarily exact. However, important trends and phenomena were observed. An attempt was made to describe the most important items to provide designers of replacement roofs with some practical data on the aging of roofing copper that has been in place from 20 to 100 years.

Some of this copper was still serviceable and other copper had been subject to leaking because of various adverse conditions. Leaks into building systems and occupied spaces usually caused

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the roof inspection. There are many roofs fabricated from copper sheets that were not inspected and are providing admirably good service in spite of their age.

Procedure

Various sites were inspected and photographs were taken of important phenomena including copper roofing sheets, flashings, gutters, fascia, downspouts, ridge caps, skylights, domes, ornamental stamped copper work, and many other items. Various types of corrosion and wear were noted. The cause of leakage was also noted and new copper work was designed for replacement where necessary. During the process of removal and replacement of the roofing, samples of typical components were retained for further study.

Table 1 lists the various buildings studied, the estimated age of the samples, and observed conditions. Table 2 lists measurements made to samples from various buildings and shows metal loss data.

The samples were taken to the laboratory, where original seams were opened. Metal thickness at original seams was compared to the metal thickness in areas of wear and pitting. This was done with a round tipped micrometer caliper.

Discussion

Corrosion and wear were related to location and use of the copper component. Copper sheet metal panels were employed in two major categories:

Type I: Those which drain immediately and are above the water line. Examples of these flashings and roof panels are as follows: counterflashings, copings, fascia, steep roof panels with standing seams and/or battens, ridge caps, sills, etc.

Type II: Those that are below the water line and/or do not drain immediately. Examples of this type are gutters, pitch boxes, copper base flashings, metal edgings which intersect with ponds on roofs, flat seam roofing, aprons, transitions, crickets (a sloping transition that prevents water running down a slope from being forced directly against a base flashing condition), slate flashings, etc.

Flashings of the first type were subject to weight loss and thinning, but were not usually affected by expansion or contraction strain. These components, when properly installed, will expand and contract in a manner that does not build up compression or tension strains. Thinning from corrosion, when uniform, extends over a long period of time and does not affect the serviceability of the panels for many decades. If, however, these panels are restrained unequally, buckling can occur. Once the material has buckled, work hardening occurs and repetitions of the strain will cause fatigue cracking in a few years. Large radius bends at changes in direction reduced cracking. Sharp bends were more susceptible to cracking.

Ridge caps, which are subject to vibration and wind flutter, can also become work hardened and will then be subject to cracking. Cracked panels are shown in Fig. 1.

Free draining sections should not be soldered on the exposed surface, if possible. If the components can be made watertight without soldering, they will last longer than if they are soldered. It is very difficult to clean fluxes and cleaning agents from the edge of the soldered seam, but they must be cleaned and neutralized. A 5 to 10% solution of washing soda or 0.5 kg (#1) of lye per ten liters (2 gal.) of water was used, followed by a washing down and thorough rinsing with clear water [1]. Figure 2 shows locations that are highly susceptible to pitting. Table 2 samples CG 1a, 2, 4 were severely pitted and showed the highest corrosion rates ranging from 4.3- μ m (0.17 mils) per year to 7.3 μ m (0.29 mils) per year.

Roof panels: Transverse joints of steep panels need not be soldered. Transverse joints of low sloped panels should be soldered on the back prior to installation so that the soldered joint can

		TABLE 1-	Buildings inv	estigated.	1	
Job name/Location	Date Built	Insp. Date	Est. Age of Copper	Type of Copper	Condition of Copper	Visual Observations
Bowers Hall, Yale University, New Haven, CT	1923	1983	50	red	pitted seams	gutters failed
435 College St., School of Music, Yale U.	1929	1983	54	red	pinholes	failed at drip lines of slate
				L.C.C.	good condition	Some split seams
Coxe Cage Field House, Yale University	1924	1981	58	red	fair to good	required expansion joints,
						coping & wall panels salvaged
Timothy Dwight College, Yale University	1933	1981	48	red	pitted through	coat of asphalt was
						detrimental
Harkness Tower, Yale University	1917	1984	67	red	pitted through	base flashing failed,
						counterflashing salvageable
Hendrie Hall, Yale University	1894	1981	89	red	counterflashing	original base flashing
					fair to good	replaced previously
Lapham Hall, Yale University	1924	1981	57	red	pitted at solder	sills eroded
Memorial Hall, Yale University	1061	1981	80	red	seams split	dome failed, panels too
					4	large, not properly fastened
Morse College, Yale University	1960	1982	22	red	good condition	Locations eroded by run off
Sage Hall, Yale University	1923	1983	50	red	pitted at	coping seams cracked;
					soldered seam	improper expansion joint
Sterling Library, Yale University	1927	1980/84	58	L.C.C.	vent panels good	failed at poor securement
Stiles College, Yale University	1960	1982	22	red	good condition	except where eroded by
						run off
Trumbull (checked color), Yale University	1929	1982	53	L.C.C.	pitted	turned green
University Dining Hall, Yale University	1901	1981	80	red	split seams,	improper securement
					cracked bands	

'ayne Whitney Gym, Yale University Voolsey Hall, Yale University	1930 1901	1980 1981	50 80	L.C.C. red	excellent failed	good workmanship only vertical wall panels could be salvared, panels not
		1000	ç	(•	secured, panels too large
ale Center for British Art, Yale University	1973	1985	12	г.с.с.	excellent-good	seams split exp.
ale Datly News, Yale University	1932	1982	20	red	gutter failed	poor work
lartford City Hall, Hartford, CT	1915	1983	68	red	gutter failed	batten roof coated with
						mastic, clerestory wall in good condition
Calvary Presbyterian Church, Enfield, CT	1965	1985	20	L.C.C.	split seams	not properly fastened, poor
						installation procedures
JGNA, 54 Elm Street, Hartford, CT	1926	1985	59	red	pitted	both nor properly fastened
				L.C.C.	pitted	L.C.C. turned green
Emanuel Synagogue, West Hartford, CT	1958	1982	23	red	pitted at seams	pitted thru from erosion at
						base flashing
aith Seventh Day Adv. Church, Hartford, CT	1922	1984	62	red	pitted at seams	pitted thru from erosion
General Instrument, El Paso, TX	1975	1983	×	red	flat seams split	seams not set and panels
					no patina	not cleated properly
Auseum of Fine Arts, Springfield, MA	1930	1981	51	L.C.C.	failed at flat	aluminum coating materials
					seam, gutter	prevented repair of copper
	0001	1001		•		
vak mili school, Bldgs 2,3,9, Hartford, CI	0661	1983	55	red	pitted at solder seams	Bldg. #2, cornice sample
00 Pleasant Valley, Rd., South Windsor, CT	1960	1983	23	red	seams split	erosion at location of run off
Seorge Vincent Smith Museum, Springfield, MA	1890	1982	92	red	pitted through	seams split
tonington Borough School, Stonington, CT	1890	1983	93	red	cracked metal	split seams
					in gutter	
samples.						

copper						
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Project Name				Thickn	ess	Average Corrosion Rate per year
Location, Approx. Age	Sample #, Type Cop.	Mode of Failure	Sample Location	Location of Measurement	SI µm (in.)	SI µm (mils)
Bicentennial, Educational Facility; Coastal/Intercity	BC #1 Red	Split seams, pitting		@ Lock @ Field	533 (.021) 508 (.020)	
Environment;	BC #2	Cracks from expan-	cartouche	@ Lap @ Eicld	508 (.020) 406 (.016)	
Approx. 80 yrs. old	Red		horizontal	@ Field @ Field	406 (.016)	1.3 (.05)
	BC #3 Red	Copper mounted on steel frame.	reduced ridge over Dining Rm.	@ Freid @ Lock @ Field	508 (.013) 508 (.020) 457 (.018)	(00.) 0.1 6 (02)
		corroded at fasteners	slope near ridge peak horizontal, 254 mm (10″) from	@ Field "A" @ Field "B"	405 (.019) 406 (.016)	
			peak vertical, 356 mm (14") from	@ Field "C"	432 (.017)	.9 (.04)
			peak slope, 560 mm (22") from peak	@ Field "D"	432 (.017)	.9 (.04)
	BC #4 Red	Solder joints	top of ridge SW shore at ridge	@ Lock "B" @ Eicld	533 (.021) 508 (.020)	
		201101	top of ridge	@ Field "A"	508 (.020)	.3 (.01)
	BC #5	Fatione at lan	305 mm (12") from top of ridge bottom of outter	@ Field "C" @ Field "∆"	508 (.020) 483 (.019)	.3 (.01)
	Red	in gutter	vertical, 305 mm (12 ") up from	@ Field "B"	483 (.019)	•••
	BC #6	Seams split, pitting,	bottom of gutter bottom of gutter	@ Field "A"	483 (.019)	:
	Ked	buckling at bottom of gutter	vertical 102 mm (4") up from bottom of outter	@ Field "B"	533 (.021)	:
			(Bit. coating removed from sam	nple BC #6)		
	BC #7	None noted, some	ı	@ Lock	533 (.021)	•
	Ked	pitting in solder noted		@ Field	483 (.019)	.6 (.02)

SL#2 None noted, some vertical LCC pitting present top of ridge LCC None noted, some vertical LCC None noted, some top of ridge LCC None noted, some isiled 152 mm (6") from ridge peak LCC Lapped solder joints 152 mm (6") from ridge peak no pitting in pitting isiled 153 mm (6") from ridge peak LCC Lapped solder joints 152 mm (6") from ridge peak no pitting in pitting isiled isiled LCC htru at other vertical castle, lower portion, LCC Pitted isile isile LCC Pitted east side lower portion, LCC Pitted cations cornice LCC Pitted Cornice cornice LCC Deep pitting Cornice cornice LCC Red CG #3 None noted rear standing seam Red CG #3 None noted near standing seam reading colder join Red CG #3 None noted rear standing		@ Lock @ Field	559 (.022) 559 (.022)	
LCC pitting present top of ridge LCC Lapped solder joints 152 mm (6 ") from ridge peak LCC Lapped solder joints 152 mm (6 ") from ridge peak Railed 152 mm (6 ") from ridge peak 0 pitting SL #4 None noted this 152 mm (6 ") from ridge peak Railed 152 mm (6 ") from ridge peak 0 pitting SL #4 None noted this vertical castle, lower portion, pitted LCC huru at other no pitting LCC None noted east side Incations CG #1A None noted Red Deep pitting Cornice LCC Deep pitting Cornice <td>tical</td> <td>@ Lap</td> <td>559 (.022)</td> <td></td>	tical	@ Lap	559 (.022)	
SL #3 None noted, some top of ridge LCC pitting present 152 mm (6") from ridge peak Lapped solder joints 152 mm (6") from ridge peak SL #4 None noted this © pitting SL #4 None noted this wertical castle, lower portion, east side LCC locations 152 mm (6") from ridge peak SL #4 None noted this wertical castle, lower portion, east side LCC httpd wertical castle, lower portion, east side LCC httpd corations LCC None noted wertical castle, lower portion, east side LCC httpd wertical castle, lower portion, east side LCC None noted wertical castle, lower portion, east side LCC Deep pitting cornice		@ Field	533 (.021)	.4 (.02)
Lapped solder joints152 mm (6 ") from ridge peak failedfailed0pittingfailed0pittingfailed0pittingSL #4None noted thiswertical castle, lower portion, vertical castle, lower portion, erast sideLCClocationswertical castle, lower portion, vertical castle, lower portion, erast sideLCCnone notedwertical castle, lower portion, erast sideCG #1ANone notedwertical castle, lower portion,) of ridge	@ Field "A"	559 (.022)	:
152 min (6 ") from ridge pead no pitting SL #4 None noted this LCC location, pitted LCC locations LCC locations LCC locations CG #1A Pitted LCC locations CG #1A Pitted LCC Deep pitting CG #1B None noted Red CG #2 LCC Deep pitting CG #3 None noted Red CG #3 None noted near standing seam Red CG #3 None noted near standing seam Red CG #4 LCC none noted Red CG #3 LCC None noted Red SW, vertical @ concentrated H#1 none noted SW, vertical @ concentrated Red SW, vertical @ concentrated Red SW, vertical @ concentrated Red Sedfer joint at Red leader to drain box Red leader to drain box	2 mm (6 ") from ridge peak @ pitting	@ Field "B"	533 (.021)	:
SL #4 None noted this vertical castle, lower portion, east side thru at other locations LCC locations east side thru at other locations CG #1A Pitted east side east side thru at other locations CG #1A Pitted east side east side thru at other locations CG #1B None noted east side east side east side thruck Red CG #1B None noted Red CG #3 None noted LCC Deep pitting Cornice LCC Deep pitting Cornice LCC Deep pitting Cornice LCC Deep pitting Cornice Red CG #3 None noted near standing seam Red CG #4 none noted SW, vertical @ concentrated Red SW, vertical @ concentrated SW, vertical @ concentrated H #2 solder joint at vertical side of drain box Red leader to drain box box "A" Red leader to drain box tail piece of leader	$2 \text{ mm} (6^{-\pi})$ from ridge peak to pitting	@ Field "C"	559 (.022)	•
LCC locations east side thru at other locations LCC Pitted LCC None noted Red CG #18 CG #18 None noted Red Cornice LCC Deep pitting CG #3 None noted Red Cornice LCC Deep pitting CG #3 None noted Red Cornice LCC Deep pitting CG #3 None noted Red Cornice LCC Beader join Red SW, vertical @ concentrated Red Inoff Name SW, vertical @ concentrated Red Inoff Red Inoff No box "A" Pader joint at vertical side of drain box No box "A" Inoff horizontal bottom of drain box	tical castle, lower portion,	@ Lock	584 (.023)	
CG #1A Pitted LCC None noted Red CG #1B Red Deep pitting CG #2 Deep pitting CG #3 None noted Red Cornice LCC near standing seam Red CG #3 None noted near standing seam Red CG #4 LCC none noted Red CG #4 Red SW, vertical @ concentrated Turoff SW, vertical @ concentrated Red SW, vertical @ concentrated Red SW, vertical @ concentrated Red In the second reader to drain box Red Isolder joint at Red solder joint at Vertical side of drain box box "A" tail piece of leader horizontal bottom of drain box	cast side	@ rield	(170.) 666	(00.) 6.
LCC CG # 18 None noted Red CG # 2 Deep pitting LCC LCC CG # 3 None noted CG # 3 None noted CG # 4 near standing seam Red CG # 4 none noted Red CG # 70 Red Cornice LCC H # none noted Red Cornice Cornice Cornice Cornice Cornice Cornice Cornice Cornice Cornice LCC H # none noted Red Cornice Red Cornice Cornice Cornice Cornice Cornice Cornice LCC H # none noted Red Cornice Red Cornice Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Red Cornice Cornice Red Cornice Red Cornice Cornice Cornice Cornice Red Cornice Corni		@ Lock	533 (.021)	:
CG # 1B None noted Red Deep pitting Cornice LCC Deep pitting cornice LCC near standing seam sead CG #3 None noted near standing seam Red CG #4 near standing seam Red CG #4 none noted Red SW, vertical @ concentrated Red leader to drain box Red leader to drain box tail piece of leader tail piece of leader horizontal bottom of drain bot tail piece of leader		@ Field,	533 (.021)	.00) 0
CG # 1B None noted Red Cornice LCC Deep pitting Cornice LCC None noted near standing seam Red CG #3 None noted near standing seam Red CG #4 near standing seam Red CG #4 deep pit @ edge of solder joi LCC None noted SW, vertical @ concentrated Red SW, vertical @ concentrated swd, vertical @ concentrated Red ILCC SW, vertical @ concentrated swd, vertical @ concentrated Red ILCC SW, vertical @ concentrated stall piece of frain box		not pitted @ Field	127 (.005)	6.9 (.27)
Red CG #2Deep pittingCorniceLCCLCCnear standing seamCG #3None notednear standing seamRed CG #4Reddeep pit @ edge of solder joinH #1none notedSW, verticalCCSW, vertical @ concentrated runoffSW, vertical @ concentratedH #2solder joint at box "A"vertical side of drain boxRedleader to drain boxtail piece of leader horizontal bottom of drain box		deep pit @ Lock	533 (.021)	
CG #2 Deep pitting Cornice LCC LCC near standing seam GG #3 None noted near standing seam Red Ge #4 deep pit @ edge of solder join LCC deep pit @ edge of solder join gedge of solder join H #1 none noted SW, vertical SW, vertical Red SW, vertical @ concentrated runoff stant box Red leader to drain box box "A" tail piece of leader		@ Field	483 (.019)	.8 (.03)
LCC CG #3 None noted near standing seam Red CG #4 LCC H #1 none noted SW, vertical Red SW, vertical © concentrated runoff H #2 solder joint at vertical side of drain box Red frain box variable of drain box for the	rnice	@ Field not	584 (.023)	•
LCCCG #3None notednear standing seamRedGG #4deep pit @ edge of solder joinCG #4deep pit @ edge of solder joinLCCdeep pit @ concentratedRedSW, vertical @ concentratedrunoffSW, vertical @ concentratedrunoffstant atRedleader to drain boxRedbox "A"tail piece of leadertail piece of leaderhorizontal bottom of drain box		pitted A		í.
CG #3 None noted near standing seam Red CG #4 CG #4 deep pit @ edge of solder joi LCC deep pit @ edge of solder joi H #1 none noted SW, vertical @ concentrated SW, vertical @ concentrated runoff SW, vertical work tail picce of leader Red leader to drain box 'A'' tail piece of leader horizontal bottom of drain box		@ Field deep pit "B"	330 (.013)	4.3 (.17)
Red CG #4 LCC H #1 none noted Red Red SW, vertical @ concentrated runoff H #2 solder joint at vertical side of drain box Red leader to drain box 'A'' tail piece of leader horizontal bottom of drain bo	ur standing seam	@ Lock	483 (.019)	:
CG #4 CG #4 LCC H #1 none noted Red SW, vertical SW, vertical Concentrated runoff runoff H #2 solder joint at vertical side of drain box Red leader to drain box tail piece of leader tail piece of leader horizontal bottom of drain box)	@ Field	432 (.017)	(£0.) 6.
LCC deep pit @ edge of solder joi H #1 none noted SW, vertical Red SW, vertical @ concentrated SW, vertical @ concentrated runoff H #2 solder joint at vertical side of drain box Red leader to drain box 'A'' tail piece of leader horizontal bottom of drain bo		@ Field	610 (.024)	•
H #1 none noted SW, vertical Red SW, vertical @ concentrated SW, vertical @ concentrated runoff H #2 solder joint at vertical side of drain box Red leader to drain box box "A" tail piece of leader horizontal bottom of drain bo	pp pit @ edge of solder joint	@ Field	178 (.007)	7.3 (.29)
Red SW, vertical SW, vertical @ concentrated SW, vertical @ concentrated runoff runoff <td></td> <td>@ Lock</td> <td>533 (0.021)</td> <td>:</td>		@ Lock	533 (0.021)	:
SW, vertical @ concentrated runoff H #2 solder joint at vertical side of drain box Red leader to drain box box "A" tail piece of leader horizontal bottom of drain bo	/, vertical	@ Field	483 (0.019)	0.7 (.03)
H #2 solder joint at vertical side of drain box Red leader to drain box box "A" tail piece of leader horizontal bottom of drain bo	<i>I</i> , vertical @ concentrated runoff	@ Field	432 (0.017)	1.4 (.06)
tail piece of leader horizontal bottom of drain bo	tical side of drain box	@ Field	533 (0.021)	:
horizontal bottom of drain bo	I piece of leader	@ Field	457 (0.018)	1.1 (0.04
" 8 .,	rizontal bottom of drain box 'B''	@ Field	381 (0.015)	2.2 (0.09

Deviced Name				Thick	thess	Average Corrosion Rate per year
Location, Approx. Age	Sample #, Type Cop.	Mode of Failure	Sample Location	Location of Measurement	SI μm (in.)	SI µm (mils)
	H #3 Red	solder joint lap failed	vent stack NE slope, northern side "A"	@ Field	889 (0.035)	
			southern side "B"	@ Field	940 (0.037)	•
	H #4	butted solder joint	"B" (bitumen coating removed)	@ Lock	559 (0.022)	
	Red	seam failed	SW slope cleaned area "A"	@ Field	533 (0.021)	0.4 (.01)
	H #5	none noted	North slope (covered with	@ Lock	686 (0.027)	
	Red		coating)	@ Field	686 (0.027)	0.0 (0.00)
Coxe Cage,	CC #1	none noted	1	@ Lock	457 (0.018)	
Athletic Facility; Coastal/Suburban	Red			@ Field	457 (0.018)	0.0 (0.00)
Environment;	CC #2	crack in panel	Lock "B"	@ Lock	533 (0.021)	
Approx. 57 yrs. old	Red	ı		@ Crack	178 (0.007)	6.2 (0.25)
			adjacent to crack "A"	@ Field	483 (0.019)	0.9 (0.04)
	CC #3	fatigue at 90° bend	unexposed flange "B"	@ Field	533 (0.021)	
	Red	upper side	Muntin, exposed flange "A"	@ Field	229 (0.009)	5.3 (0.21)
	CC #4	fatigue at 90° bend	unexposed flange "B"	@ Field	533 (0.021)	
	Red	upper side	Muntin, exposed flange "A"	@ Field	178 (0.007)	6.2 (0.25)

TABLE 2-Continued.

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Borough School, Educational Facility:	BS #1 Red	crack	127 mm (5 ") From peak ridge can near neak at crack	@ Field @ Field	508 (0.020) 203 (0.008)	3.27 (0.13)
Coastal/Rural			trade and more hear at an age.			
Environment;	BS #2	none noted	gutter	@ Field	508 (0.020)	:
Approx. 93 yrs. old	Red)			
	BS #3	none noted	top of ridge	@ Field	508 (0.020)	:
	Red		$102 \text{ mm} (4^{\circ})$ from top of ridge	@ Field	533 (0.021)	÷
Calvary Presbyterian	CPC #1	none noted	horizontal gutter bottom	@ Field	660 (0.026)	
Church;	LCC		vertical 102 mm (4") up from	@ Field	660 (0.026)	•
Inland/Rural			gutter bottom			
Environment;						
Approx. 20 yrs. old						
Museum of Fine Arts,	MFA #1	none noted		@ Field	635 (0.025)	•
Educational Facility;	LCC					
Inland/City						
Environment;						
Approx. 51 yrs. old						
Sage and Bower Hall,	SB #1	erosion (wear)	vertical; 305 mm (12") from low	@ Field	483 (0.019)	÷
Dormitory Facility;	Red		point "B"			
Coastal/Intercity			valley of slate roof; horizontal	@ Field	406 (0.016)	1.5 (0.06)
Environment:			low point of vallev "A"	I		
Approx. 50 yrs. old			3 mm (1/8") from wear thru "C"	@ Field	102 (0.004)	7.6 (0.30)
NOTE: Red stands for plair	n uncoated copp	ber, LCC stands for lead	coated copper.			

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FIG. 1-Coxe Cage, 58 years old, fatigue cracking from wind.



FIG. 2—Woolsey Hall. 80 years old. Repair with aluminum coating did not stop pitting or leaks. Note: Concave edge of solder, most severe pitting. Red copper, 16 oz.

be protected from the elements and will be less susceptible to pitting. Figure 3 shows replacement panels that were presoldered so that the entire run could be locked in with the seams not exposed.

Copings: Figure 4 shows that flat or low sloping portions of copings appear to wear at a much greater rate than the vertical sections of the same piece of metal.

Skylight components: Exposed portions of muntins as in Fig. 5 were worn through, but leaks were minor because of the steep slope and condensation gutters in mullions.

Slate valley copper, as in Fig. 6, has been worn through in fifty years by localized dripping.



FIG. 3—Woolsey Hall, 80 years old. Red copper 16 oz. Dome was also replaced. Ornamental components were salvaged.



FIG. 4—Sterling Library, 58 years old. Lead coated copper. Note green patina on flat surface, lead intact on vertical surface.



FIG. 5-Coxe Cage. 58 years old. Red copper 16 oz. Skylight muntin worn through.



FIG. 6-Sage Hall. 50 years old. Red copper 16 oz. Step flashings Valley copper under slate worn out by erosion due to water run off and dripping.

Even when the above experience pinholes, pitting, and cracked joints, the quantity of water which enters the system is usually minimal because of the free drainage and rapid runoff. Such leakage may sometimes be controlled by proper placement of underlayment felts at the time of construction. However, when snow and ice are on the surface, as in Fig. 7, leaks can be quite serious.

Type II: Copper components such as gutters are much more susceptible to all of the above mentioned types of corrosion, metal thinning, pitting, pinholing, or fatigue cracking. All can cause failure of the copper gutter. Once the gutter fails, massive leaking can occur, the severity



FIG. 7—Sterling Library, 58 years old. Lead coated copper. Note pitting and white lead oxide, green color on flat portion.

of which is dependent upon the size of the watershed. Even a small hole in the gutter, such as a pinhole placed in a location where the gutter contains a puddle, will allow water to accumulate below the gutter within the substrate to the hydrostatic level of the top of the water in the gutter. In winter, gutters are quite frequently full and adjacent ice dam heights can cause large hydrostatic heads, as in Fig. 8. Underlayment felts are usually not effective in reducing the quantity of leaks in the vicinity of gutters and aprons.

Increasing the thickness of the metal at gutters was effective in prolonging the life of the various gutters inspected. Expansion and contraction strains work in a similar manner to free draining copper panels. However, in the case of gutters, even the smallest crack will allow large quantities of water to enter the system.

The soldered seams of gutters are also susceptible to expansion and contraction forces. Soldered seams must be designed and riveted in a manner that will prevent the seam from becoming the weak link in a particular gutter system. As pitting, pinholing, and thinning down of the joint adjacent to the solder occurs, less metal is available to resist expansion and contraction strains. At some point the metal shown in Fig. 9 failed by buckling at several places. Properly placed and designed gutters which allow free movement of the sections lasted much longer than those that were not properly placed or designed [2].

Aprons: Aprons are usually employed as a transition between the gutter or eave and sloping roof panels. If an apron had been employed at the battens in Fig. 9, leaking from erosion at the bottom of the battens would not have necessitated replacing the battens. The apron would have allowed increased service of the system even though some components had failed. Installation of aprons allows extended service of the copper roof system.

Large quantities of water drain from sloped roof areas whether they be copper panels, shingles, or slate. These quantities of water drip off of the components above and increase the wear at the drip line at base of the slate in Fig. 10.



FIG. 8-Commons Dining Hall, 80 years old. Red copper 16 oz.



FIG. 9-Dining Hall, 80 years old. Red copper 16 oz. gutter not cleated, tied in only at outside edge and lock at bottom of slope.



FIG. 10-435 College St., 54 years old. Red copper 16 oz. pitted through at slate drip line.

Note that these copper panels wore through in a much shorter period of time because of the accelerated corrosion caused by the dripping and erosion process. The service life of aprons and base flashings exposed to this type of corrosion can be greatly extended by placing a wear strip over the section subject to dripping. Figure 11 shows severely pitted lead coated copper from Sterling Library.

The west end of the Commons Dining Hall at Yale University experienced rapid metal thinning of the steep batten seam copper panels in the area adjacent to the incinerator. Combustion products in this vicinity definitely accelerated the corrosion. It is interesting to note that where oily or greasy contaminants hardened on the surface of the panels, these were protected and



FIG. 11-Sterling Library. ×20 micro photo of severely pitted lead coated copper.

resulted in raised islands of copper amid the unprotected panels which had thinned down. Thinning as shown in Table 2 ranged from 0.3 μ m 1.6 μ m (0.01 to 0.06 mils) per year. This range is greater than corrosion rates shown by Costas [3].

Flat seam copper panels: The size and joint configuration of flat seam copper panels is extremely important. Heavier gauge panels gave much better service life compared to thinner panels. Since the entire perimeter of each panel must be soldered, the mode of failure here in red copper panels was usually pitting adjacent to the soldered seam. In lead-coated copper panels, failure also occurred from pitting, but the seam areas were not susceptible to this pitting because of the protection from the lead coating and pretinning.

Where flat seams were properly malleted and set prior to soldering, the soldered seams were more able to resist expansion and contraction strains. Failure of lead-coated copper panels occurred where abrasions wore through the lead coating and allowed pitting to proceed at a faster rate.

Vertical standing seam lead-coated copper panels showed virtually no wear after 50 years at Payne Whitney Gym. Exposures to north, east, south, and west did not seem to affect the panels. However, vertical wall panels, at Sterling Memorial Library were only susceptible to wear when the wood slat retaining panels failed because of water entrance through the exterior of the masonry wall. The retention strips rotted out after 50 years; the copper panels became loose and were able to flex in the wind. They were cracked by fatigue. Figure 12 shows several cracked panels.

The copings at Harkness Tower were fabricated from red copper. The pitting as shown in Fig. 13 is much more severe than the lead coated copper at Sterling Library. The copper at Harkness is approximately 67 years old versus the 58-year-old copper at Sterling. However, the difference in age of nine years does not reasonably account for the great difference in corrosion.

Bronze snowguard brackets were in excellent condition after 80 years.



FIG. 12—Sterling Library, 58 years old, 16 oz. lead coated copper. Securement rotted and allowed excessive flutter.



FIG. 13-Harkness Tower, 67 years old.

Conclusions

Vertical 0.4536 kg (16 oz.) lead-coated copper panels can easily exceed 100 years of good serviceability. However, panels must be properly secured in accordance with industry recommendations or premature buckling, cracking, or displacement from the substrate can occur. The only problems observed with these vertical panels were caused by improper securement.

Vertical 0.4536 kg (16 oz.) copper wall panels in which patina formation occurred resisted degradation very well. Again, proper attachment to the substrate is of the utmost importance. Where these panels were observed in areas subject to high waterflow from other watersheds, susceptibility to erosion was noted. Protected areas can be serviceable for over 100 years, whereas areas subject to waterflow may have serviceable life spans considerably shorter. Lead coating appeared to be well worth the additional cost over and above the plain copper for vertical panels in areas subject to erosion.

Low sloping panels: Low sloping panels were most susceptible to corrosion at locations of soldered seams. Lead-coated copper showed much better resistance to pitting at soldered seams.

Pretinning of both lead coated copper and red copper prior to soldering protected the zone adjacent to the soldered seam and slowed pitting. In some cases the pitting started only at the outer edge of the tinned area. Red copper seams to be soldered should be tinned at least 25.40 to 38.1 mm (1 to 1.5 in.) beyond the area where solder will flow.

It is extremely important to clean soldered seams after soldering to neutralize the affects of fluxes and cleaning agents. Comparison of seams with adjacent exposure at various locations on the same roof showed great differences in the degree of pitting. These differences appeared to be caused by workmanship and cleaning procedures.

Roof panels that were properly restrained provided much better serviceability than those that were improperly restrained. Flexing caused by wind flutter produced work hardening and fatigue cracking.

The presence of combustion products, power plant effluent, and/or incinerator products greatly accelerated the rate of corrosion on roof panels downwind of the contaminant.

Heavier gauges of copper such as 0.567 kg (20 oz.) and 0.6804 kg (24 oz.) appear to be well worth the added cost for materials, especially on flat and low sloping sections such as gutters, aprons. base flashing, and other components that have portions below the water line.

Copper flashings and other components used in conjunction with slate should be no less than 0.567 kg (20 oz.) and lead coated wherever possible. Slate has a greater life span than that of 0.4536 kg (16 oz.) copper. For best results, heavier copper should be used with slate to reflect the long-term use of the slate roof system. Lead coating also retarded the initiation of erosion and pitting at drip lines adjacent to the slate.

Supplementary strips at drip lines were effective in protecting copper flashing from erosion at these locations.

In general, lead coating improved serviceability of the properly installed copper panels.

The most important factors in extending the life of copper roofing and flashings were proper installation procedures, good detailing, and good design. Our observations of prematurely failed copper components were almost always attributed to improper workmanship, improper design. or the presence of an external contaminant.

Reduction in copper thickness caused by long-term atmospheric corrosion appeared to be less important than the pitting of small areas.

Components such as gutters, which were subjected to expansion and contraction forces, were susceptible to buckling at locations where metal had been thinned by corrosion.

25.4-mm (One-inch) diameter brass pipe used in conjunction with snow brackets was severely dezincified and cracked at 80 years of age (Fig. 14). Copper pipe is a better choice than brass for snowguard use.

Fasteners: Copper and bronze roofing nails were in excellent condition. Corrosion affecting serviceability was not observed. However, where galvanized or steel fasteners were employed, many of the fasteners disintegrated and allowed premature flutter and displacement of the copper panels.



FIG. 14—Snowguard pipe. \times 40 micro photo, Commons Dining Hall. Eighty years of exposure caused this brass pipe to crack and loose its tensile strength. Visual appearance is severely pitted.

Roofing panels for low sloping, steep sloping, and vertical application fabricated from heavier gauges of copper gave excellent serviceability even with somewhat increased panel widths.

Surface treatment: Washing and neutralizing improved the appearance of copper panels and shortened the time to acquire an even patina by one to two years in some locations observed. (Physical samples were not available from these sites).

Lead coated copper panels on flat to up to 45° slopes acquired a green color after 25 to 30 years of exposure. The color on lead-coated copper was more blue-green, while the patina on plain copper was more toward the yellow-green in appearance.

At many sites where improper repairs had been attempted by applying asphaltic or aluminum coatings, these coatings were found counterproductive. Once they were applied, individual soldering and replacement of panels was almost impossible. Do not apply these contaminants to copper.

At many locations where lead-coated copper panels were abraded during installation, pitting progressed at a faster rate.

Properly soldered joints with a minimal quantity of solder resisted pitting much better than joints that had excess solder quantities. Where the outside edge of the solder was smooth or concave, there was less pitting than at locations where the solder was convex. Convex solder edges produced a reentrant crevice at the base of the solder.

Acknowledgment

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DISCUSSION

*R. Baboian*¹ (discussion topic)—Green patina is usually associated with architectural copper. However, I would not expect this behavior with lead-coated copper. It is common to find a green coloration on lead-coated copper.

H. Fishman (author's closure)—Perhaps the term green patina should not be used in the same context on lead coated copper as it is used in architectural red copper. The green patina is principally brochantite, a form of copper sulfate. The lead coated copper observed started out as a bright gray, turned darker gray, and portions of it later acquired a very dull finish, and in some locations a white powder formed on the surface.

Lead coated copper which was observed in excess of thirty years old acquired a green-gray cast. Older lead coated copper turned completely green, but in the more gray range than the red copper.

¹Texas Instruments, Attleboro, MA.

We do not have the facilities for, nor have we tested this material. However, we do have samples available should somebody be interested in testing same.

A probable answer for this phenomena is that the lead coating becomes thin in some areas and the copper shows through. The copper then forms the patina probably similar to brochantite. The green color then leaches into the white and gray components attached to the surface of the lead in other locations.

R. Baboian¹ (discussion question)—Your comment about new copper not lasting as long as old copper is an interesting one. Would you elaborate on that subject?

H. Fishman (author's closure)—An inspection was made at the Yale Daily News which had various copper valleys and gutter components. They were in service for an estimated fifty years. They were fabricated from lead coated copper and were in very good condition. However, on the south side of the building, there was a red copper gutter which had acquired a dark brown color but showed no evidence of patination. The building superintendent stated that it had been replaced five years previously. This gutter was in poor condition and exhibited signs of pitting at the bottom termination adjacent to the drip line of the slate roof. The areas where this pitting occurred were very bright red color.

Environmental Degradation of Telecommunication Hardware

REFERENCE: Lee, T. S. F., Healey, N., and Trumble, W. P., "Environmental Degradation of Telecommunication Hardware," *Degradation of Metals in the Atmosphere, ASTM STP 965,* S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 115-124.

ABSTRACT: This paper is a survey of the corrosion problems encountered in Bell Canada's telecommunication hardware. Specifically, the environmental attack on the outdoor metallic equipment will be addressed. These metallic parts include outdoor connectors, guy strands, lashing wires, guy hooks, cabinets, and manhole equipment. To be presented are the results of material analyses, failure analyses, field testing, and accelerated laboratory testing, which include a number of investigative programs undertaken in the previous years.

KEY WORDS: hydrogen embrittlement, stress concentration, stress corrosion cracking, sensitization, galvanic corrosion, fretting corrosion, atmosphere, telecommunication hardware

Various metallic parts are used in the outside plant of Bell Canada. Most of the hardware has been designed with certain degrees of corrosion prevention. Some of these practices may involve protective coatings and encapsulants, some may involve the use of corrosion resistant metals and alloys, and some may be controlling the environment in hardware cabinets. Unfortunately, totally reliable corrosion prevention practices often cannot be achieved. This is partly due to the complexity of the field environments and some basic corrosion mechanisms, and partly because a trade-off has to be made among corrosion prevention, other performance requirements, and costs. As a result, corrosion has been, and will increasingly be, a concern for Bell Canada's telecommunication equipment.

Over the past decade, much research conducted by Bell-Northern Research (BNR) and Bell Canada has focused on the study of corrosion and corrosive environments. Many reports have been issued on this once low priority issue. The following is a synopsis of the studies conducted by Bell-BNR in an effort to protect the telecommunication hardware and combat against corrosion failure.

Survey of Corrosion Problems

Lashing Wire

The outside plant equipment is particularly susceptible to corrosion attack because of the hostile atmosphere and underground environments. One example of atmospheric attack is the premature failure of stainless steel lashing wires [1]. Lashing wires are used to secure aerial

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transmission cables to the pole line structure. The combination of corrosive species from the atmosphere, moisture condensation, and applied tension may cause stress corrosion cracking of the stainless steel wires. (Stress corrosion cracking occurs when a metal cracks after being subjected to a constant tensile stress and exposed simultaneously to a specific corrosive environment for a given time.) This is especially prominent if the wires have not received a proper heat treatment. Instances of lashing wire failure caused by this type of attack have been experienced [1].

Steel Guy Strand

At the ends of a pole line structure, galvanized steel guy strands are used to provide mechanical support to the structure. Failure of guy strands has been reported, resulting in costly repair and safety concern. Laboratory investigation has indicated that the failure is caused by hydrogen embrittlement assisted by localized wearing [2]. Hydrogen can be generated by galvanic corrosion reactions at the stress concentration sites.

Connectors and Outdoor Cabinets

Even in confined environments, such as inside the outdoor hardware cabinets, corrosion still prevails. Connectors with inadequate design have been found to suffer contact resistance increase after six years of field exposure, which could result in noisy telephone lines or even line disruption. The cause of this connector failure is fretting corrosion on the contacting metallic surfaces [3]. Another problem associated with connector corrosion is short-circuiting of adjacent connectors. The problem arises as corrosion products, combined with atmospheric contaminants and moisture condensation, bridge over adjacent connectors [4]. The result is the so-called "cross-talk" phenomenon.

Corrosion of the outdoor cabinets themselves is also a concern. Most of these cabinets are built with painted steel plates. Various protective paints have been used to protect the steel cabinets against the atmosphere. However, long-term exposure to sunlight, plus high temperatures and humidities, may cause the paint to deteriorate, resulting in localized corrosion attack on the underlying steel. In some areas of the cabinet, stainless steel fasteners are applied on the mild steel plates. This coupling of dissimilar alloys has been found to promote galvanic corrosion on the less noble steel plates [5].

Underground Equipment

The aforementioned corrosion phenomena are some examples of corrosion attack from the atmosphere. However, the corrosion issue does not end here. Beneath the ground line there is underground equipment, such as those inside the manholes, and there is buried hardware, such as buried cables and earth anchors that are in direct contact with the ground soil [6]. In the manholes, various types of electrolytic corrosion are prevalent because of the frequent flooding in the manholes. The use of road salt in the Canadian winters further promotes this problem.

Galvanic corrosion of equipment submerged in flooded manholes is an important concern. In this corrosion mode, galvanized steel racks, ladders, and so forth are usually the vulnerable parts because they are often the anodic sites of galvanic corrosion reactions [7]. On the other hand, the cathodic parts are not always exempted from corrosion damage because of the generation of electrolytic hydrogen on their surfaces. In a field trial, some stainless steel V-band clamps were found to crack, and the cause was attributed to hydrogen embrittlement [8].

Another important underground corrosion phenomenon is stray current corrosion. Some galvanized steel cable racks inside the manholes were found to be severely corroded in four years (Fig. 1). The cause has been traced to stray currents from nearby electric railtracks. Bell Canada recently is planning to install underground transmission cables alongside the Trans Canada



FIG. 1—Corroded manhole cable rack after 4 years of field exposure. Note: the corrosion was due to stray currents from nearby electric railtracks in Toronto.

Pipeline. In this layout, stray current corrosion of the cables will be a big concern since a relatively large impressed current is being used on the pipeline for cathodic protection.

Pole Line Hardware

It should be noted that not all outdoor equipment is subjected to corrosion failure. In fact, a large number of outdoor metallic parts are still performing their function beyond their life expectancy. BNR has recently carried out an analysis on samples of horizontal steel strands from pole line structures. It has been found that the mechanical properties of these strands still match the specified values after 55 years of field exposure. Spectroscopic analysis has shown that the corrosion product formed on the surface of these strands is typically iron oxide, which has been acting as a protective layer to prevent further corrosion on the underlying steel wires. Moreover, the steel bolts fastened on wood poles has been found to have minimal corrosion attack after over 30 years of field exposure (Fig. 2). The encouraging fact is that these bolts were not only exposed to the atmosphere, they were also in contact with the wood poles that had been treated with once suspected corrosive chemicals.

Having briefly surveyed Bell Canada's corrosion problems, attention is now turned to describing some corrosion investigations and remedial measures in detail.

Stress Corrosion Cracking of Lashing Wires

Lashing wires [1] used by Bell Canada for supporting aerial cables in position are presently made of American Iron and Steel Institute (AISI) Type 430 stainless steel. Failure of lashing



FIG. 2-Pole bolt after 30 years of field exposure.

wire to support the aerial cable could result in a potentially disastrous situation. During the period August to December 1978, lashing wires received by the Quebec Region from one of the vendors showed severe brittle fractures in the field. Since only one batch of lashing wires was found to have such failure, it was suspected that the particular batch had received improper heat treatment, rendering the wires susceptible to stress corrosion cracking. Bell-Northern Research was alerted of these failure instances, and an investigation was mandated to find out the failure mechanism of the lashing wires and to recommend remedial action. Specimens failed in the field were retrieved to BNR. Their microstructures were examined, and tensile strength and ductility were measured. Experimental specimens were also analyzed in the same way after being subjected to various heat treatment schemes. The purpose was to simulate the material condition of the field specimens by varying the heat treatment parameters and to compare these parameters with those stated in the product specification.

The following were three important observations on the field samples:

1. The lashing wires failed by intergranular cracking after short periods in the field (Fig. 3).

2. The grain boundaries of the recrystallized structure of the wires showed heavy precipitation of chromium carbides (Fig. 4).

3. Slight rusting occurred in areas near the intergranular cracks.



FIG. 3—Typical appearance of crack in Quebec Region lashing wire. Note: Cracking takes place only along the grain boundaries where the chromium carbide is present. This type of crack is called intergranular cracking. Magnification $\times 225$.



FIG. 4—Typical microstructure of lashing wire that failed in Quebec Region. Magnification $\times 1000$. Note: the thick lines show precipitation of chromium carbide at the grain boundaries. In a nonprecipitated specimen, the boundaries would all appear as fine lines as can be seen at some borders above.

The mechanical properties of the field samples are shown in Table 1.

Experimental samples were prepared to simulate field sample conditions. This was done by annealing the cold-drawn wires at a constant time but at different temperatures, namely, 677, 829, and 1093°C. The mechanical properties of these specimens are listed in Table 2.

When the wire was annealed at 677° C the microstructure showed very little change from that of a drawn structure with elongated grains. The wire in this condition was hard and brittle (Table 2). None of the specimens from the field exhibited a nonrecrystallized microstructure; hence, all field specimens examined must have been annealed above 677° C.

When the wire was annealed at 829°C the microstructure consisted of equiaxial grains of ferrite and randomly dispersed particles of chromium carbides. The structure was desirable

History of Wire	Yield Point, N	Tensile Strength, N	Percentage Elongation, %
Specimens taken from	401	570	
Grandby Quebec	307	570	27
Grandoy, Quebee	379	566	28
	379	566	26
	379	566	25
Average	386	566	26
Specimens taken from	379	557	33
Gatineau, Quebec	379	561	32
	383	557	32
Average	379	557	32
Specimens taken from	388	552	24
Telecommunications House	365	548	31
	379	548	29
	379	548	26
Average	383	548	27

TABLE 1-Mechanical properties of field lashing wire specimens.

History of Wire	Yield Point, N	Tensile Strength, N	Percentage Elongation, %
Wires annealed at 677°C	713	878	4
	713	793	2
	748	802	2
	722	793	2
Average	722	815	2
Wire annealed at 829°C	347	557	28
	347	557	28
Average	347	557	28
Wires annealed at 1093°C	526	748	18
	512	748	20
	526	757	18
Average	521	753	19

TABLE 2-Mechanical properties of experimental lashing wire specimens.

since it showed minimal precipitate in general and the precipitate that was formed at the grain boundaries was discontinuous, thus minimizing the susceptibility to intergranular corrosion. The tensile properties of the wire annealed at 829°C were the closest to those of the field specimens (Tables 1 and 2), but the field specimens had much more abundant grain boundary precipitate.

When the wire was annealed at 1093° C, it showed a slight grain growth. Chromium carbides were found at the grain boundaries as well as in the grains. The wire was harder and more brittle than when annealed at 829° C. This was a result of the so-called high temperature embrittlement (>1000°C) for ferritic stainless steels due to the precipitation of carbonitrides [9]. Since the mechanical properties of the field specimens were not comparable to those of the 1093°C annealed wire, it suggested that the field specimens were heat treated at a lower temperature.

The above observations led to the conclusion that the failed field specimens were annealed at a temperature higher than the desirable temperature of 829°C, but below the temperature range (1000°C and above) that would cause high-temperature embrittlement. In particular, it is known that when ferritic stainless steels are annealed above 925°C, sensitization will occur regardless of the subsequent water quenching or air cooling [9]. This occurs because at 925°C or above, the alloy matrix will dissolve a large part of the existing carbides (and nitrides). In subsequent cooling, chromium carbides and nitrides will rapidly precipitate at grain boundaries, leaving a zone depleted in chromium near the grain boundaries. In this regard, the alloy becomes susceptible to intergranular corrosion, and will crack intergranularly when under tension.

The vendor of the inferior batch of lashing wires was alerted of this problem and traced it back to an uncontrolled furnace. This furnace was then replaced. In addition, ASTM Recommended Practices for Detecting Susceptibility to Intergranular Attack in Ferritic Stainless Steels (A 763) was added to the product specification to protect future lashing wires from the above mentioned attack. Since then, no more field failure has been reported.

Hydrogen Embrittlement of Guy Strands

Steel guy strands [2] are used to secure the aerial cable structure (pole line) at both ends. At the end pole of the structure, a guy strand is placed in tension between the top of the pole and the ground (via an earth anchor) at approximately 45°. The strand is made of galvanized AISI

1060 mild steel wires. In order to avoid stray currents being transmitted to the pole system from the ground, a ceramic insulator is placed between the upper and lower guy strands. Two guy grips of the same steel grade are looped around the insulator, and the grips are in turn connected to the upper and lower strands.

In the field, about ten instances of guy strand failure were experienced by Bell Canada. In particular, the breaking location was always at the loop of the guy grip in contact with the insulator. Such failure would not only cause telephone line disruption, but also cause public hazard as a result of potential pole structure collapse.

Again, BNR was alerted of the problem, and an investigative program was carried out. A pilot pole line structure was built on BNR premises and various loads were applied to the structure to determine whether the guy strands would fail. It was concluded from this work that pure tensioning under all reasonable situations could not cause the newly installed guy strands to fail.

A lab investigation was also undertaken to determine the mechanical or environmental causes for the failure. In this program, guy strand field specimens from the Ontario and Quebec regions were randomly collected for analysis. Virgin specimens were also obtained for baseline measurements. The details of this work are described as follows.

Stress Concentration

Visual examination for all specimens received from the field was carried out to determine whether any dimensional characteristics of the guy specimens were a contributing factor for field failure. The most important observation was that all the ceramic insulators examined have ridged shoulders that would create stress concentration on the guy grips. The sharpness of these ridged shoulders was measured to be at a 156° angle and 0.033 cm radius. This stress concentration was found to cause various degrees of damage to the guy grips in the field, ranging from flattened and abraded wires, to notched and even broken wires.

Mechanical Testing

Simple tension testing was carried out to measure the strength of a guy specimen and to detect where the weakest point was in the specimen. By its nature, it directly indicated how well the guy strand performed under over-tensioning. In addition, cyclic tension testing was performed to stimulate the cyclic loading induced on the guy strands caused by storm and thermal loading. Load frequencies in the range of 0.3 to 3.0 cycles/second were used, together with various load amplitudes and load levels. Results indicated that both types of testing could not duplicate the failure mode of the guy strands that happened in the field. In almost all test cases, the ceramic insulator shattered before any failure of the grip, whereas in the field, it was found that failure occurred on the grip at the point that was in contact with the ridged shoulder of the insulator. This indicated that the stress concentration at the insulator shoulder could not cause grip failure in simple over-tensioning or cyclic tensioning alone.

The lateral vibration test was performed to simulate the effect of relative micromovements between the grip and the insulator shoulder caused by wind-blow against the guy strand in the field. These micromovements were suspected to cause wear or notching on the grip wires in contact with the insulator shoulder. Virgin guy specimens cut to a gauge length of 2 ft (0.6 m) were first tensioned to a constant load of 17.8 kN. A motor cam was then used to cause lateral vibration at the center (that is, the insulator) of the specimens at a frequency of 28 cycles/s for a number of cycles in the range of 50 000 to 450 000 cycles. The half amplitude of the lateral movement was set either at 2.5 or 5.0 mm. These settings were calculated to simulate strand resonance caused by severe wind-blow in the field. After the vibrational cycles, the specimens were failed in a simple tension test. Results indicated that in all cases some grip wires were broken at the insulator shoulder before the shattering of the insulator. Therefore, lateral vibra-

tion could initiate grip failure at the insulator shoulder and thus simulate the field failure mode of the guy strands.

Hydrogen Embrittlement

Because of the wearing of the galvanized coating of the steel grip wires occurring at the insulator shoulder, electrolytic hydrogen was suspected to be generated on the exposed steel sites by means of some galvanic corrosion reaction when the grip wires were wetted during rainfall or under high humidities. If hydrogen was indeed formed, it would likely embrittle the grip wires at the insulator shoulder and hence promote premature failure. Hydrogen testing was performed on specimens with a pair of single grip wires fitted to a ceramic insulator. The galvanizing coating in the region contacting the insulator shoulder was removed by a file. The wires were then charged with hydrogen in the 0.1 N sulfuric acid (H_2SO_4) electrolyte at a charging current of about 3.5 mA/cm² for about 10 h. The specimen was finally failed in a simple tension test. The results showed that hydrogen indeed could embrittle the guy grips. A 14% reduction in tensile strength was caused by the hydrogen charging in both virgin and field specimens. This is considered to be a conservative estimate, since hydrogen outgassing was likely to occur between the completion of hydrogen charging and the tension test. At any rate, in addition to stress concentration at the ridged shoulder of the insulator and wearing of the grip wires at the shoulder, hydrogen generated therein by galvanic reactions could further promote guy strand failure.

Based on the above test results, the mechanism of the guy strand failure in the field was formulated. The ridged shoulder of the ceramic insulator acted as a stress raiser on the guy grip. Because of resonance induced by wind-blow in the field, relative movements between the insulator surface and grip wires occurred, and the sharp shoulder of the insulator caused wearing and notching on the grip wires. Once the galvanizing coating of the wire was worn off at the shoulder, local galvanic reactions generated hydrogen on the exposed steel areas, and embrittled the steel. The coupled mechanical wearing and environmental degradation of the grip wires would eventually result in complete failure. Although the phenomenon seemed complicated, the solution was relatively simple. Bell Canada has changed the insulator design and eliminated any ridged shoulders, and no further failure has been reported since then.

Fretting Corrosion of Connectors

Fretting corrosion occurs when corrosion reactions on two contacting metal surfaces are promoted or enhanced by the occasional oscillatory relative motion (fretting) between the surfaces. Fretting corrosion is often characterized by the removal of corrosion debris by fretting and subsequent formation of further corrosion products. In a connector, the fretting action arises because of differential thermal expansion between the connector clip and the conducting wire. Daily and seasonal change in temperature in the connector's environment causes this differential thermal expansion. The corrosion products are mostly abrasive metal oxides formed by atmospheric attack. Outdoor exchange connectors that are subjected to fretting corrosion will have significant contact resistance increase, resulting in noisy line signals or even line disruption. Good connectors are often designed to have sufficient normal force on the metallic contacts to retard the fretting action, and hence to prevent fretting corrosion.

Six types of connectors were field tested by BNR to determine their susceptibility to fretting corrosion. They were housed in outdoor cabinets in four different geographical locations for over six years. Their contact resistance was monitored every six months in order to detect the occurrence of fretting corrosion. The results indicated that one type of the connectors showed significant increase in contact resistance as the exposure time increased. Connector specimens after the field exposure were retrieved and subjected to microsectioning and microscopic analysis. It was found that the contacts of the connectors that showed high contact resistance increase in the field were damaged by fretting corrosion. The tin plating at the contact between the phosphor bronze connector clip and the copper wire conductor had numerous worn areas. Besides the predominant oxides, sulfates were also found as corrosion products in some areas of the damaged contacts. A layer of atmospheric dust was found to deposit on the field exposed connectors. Chemical analysis of this dust indeed indicated that it contained as much as 8% sulfates. In addition, copper was found to diffuse from the conductor to the tin plating. In some areas, as much as 30 to 50% copper was detected in the tin plate. This diffusion would promote the formation of Cu_6Sn_5 and Cu_3Sn intermetallic compounds. These compounds are known to be hard and brittle, and would enhance the fretting damage at the contact.

The fretting corrosion damage on connectors was also simulated in the laboratory. In that, connectors were subjected to thermal cycling between -40 and $+60^{\circ}$ C in an environmental chamber. Again, the particular type of connectors that had shown failure in the field test also failed in the thermal cycling test. Although the atmosphere in the laboratory was less corrosive than in the field, fretting corrosion was the predominant mechanism for the contact resistance failure in the laboratory, because oxidation of the contact metals still prevailed in the indoor atmosphere.

Future Plans on Corrosion Prevention

In the coming year, Bell-BNR will devote much effort in understanding the environments in the Bell Canada operating regions. Since the atmosphere varies from one area to another, global data on the atmosphere cannot be applied practically to fight atmospheric corrosion. For the past seven years, BNR has been monitoring the local changes in temperature and humidity inside the outdoor hardware cabinets. These cabinets have been installed in various regions so that a representative specimen can be obtained. Recently, a program has also been started to collect specimens of dust and gases from the atmosphere in different areas. Future analysis of these specimens will help Bell-BNR engineers to gain better understanding of the corrosion problems and to take precautions in their hardware designs and materials selection. In addition, before the launch of the large-scale project of installing transmission cables alongside the Trans Canada Pipeline, it is anticipated that much design and engineering effort will focus on corrosion provention procedures.

Conclusions

This paper has briefly surveyed various corrosion problems encountered in Bell Canada's outside plant environments. Some investigative projects and remedial actions have been described in detail. These detailed descriptions were selected to address different atmospheric corrosion mechanisms on telecommunication equipment, namely, stress corrosion cracking, hydrogen embrittlement, and fretting corrosion. Obviously, this is only a partial list of the Bell-BNR effort to combat corrosion. As more and more sophisticated and expensive telco equipment is placed in the field, corrosion will be an increasing concern. No ingenuous design or advanced equipment will perform its function if it cannot reliably stand up in its environment.

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Long-Term Corrosion Behavior of Materials in the Marine Atmosphere

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ABSTRACT: The relative corrosion resistance for numerous materials of interest to architects and engineers as well as the marine construction and automotive industries are presented. Results of exposures in the natural marine atmosphere at Kure Beach, NC, for up to 45 years are included for steels, stainless steels, aluminum alloys, copper, nickel, and titanium alloys.

KEY WORDS: marine atmospheric corrosion, stress corrosion, long-term corrosion

Investigations of the corrosion behavior of various materials in marine atmospheres were initiated in the 1940s when it was recognized that corrosion data from exposure in natural marine environments were essential. These early exposures provided valuable information on the marine corrosion resistance of many materials and set the groundwork for standardizing atmospheric corrosion testing. Some samples from these first test programs are still on exposure at the LaQue Center's marine atmospheric test sites at Kure Beach. Other tests started after these first programs are also still providing long-term data.

Corrosion or deterioration of materials used in atmospheric environments containing the chloride ion (for example, ship decks, sea platforms, seashore installations, recreational equipment, automobiles, and so forth) is a major concern as materials and replacement costs continue to spiral. These areas account for a significant portion of the estimated cost of \$168 billion in 1985 for corrosion in the United States. Industry is actively pursuing methods and materials that will give greater service life to both structures and machines.

There are a number of corrosion control methods that can be employed, one or more of which can be used to give greater service life:

- (1) selection of more resistant materials,
- (2) improvement of design,
- (3) protective coatings for material surfaces subject to corrosion,
- (4) treatment of the environment, and
- (5) continued maintenance.

Obviously, the choice of materials for use is not based solely on corrosion resistance. Mechanical and physical properties, as well as economics, play major roles in the selection process. The corrosion resistance of a material is nonetheless an important component in the final choice since it will impact both economics and mechanical properties over the lifetime of the product or structure.

It is the purpose of this paper to present, chronologically, results from long-term corrosion

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and stress corrosion tests of several materials in marine atmospheres. Some of the factors that will influence the atmospheric corrosion behavior of materials are also addressed. These data are from exposures in the aggressive marine atmospheric test sites at Kure Beach (Fig. 1) for exposure periods up to 45 years.

Kure Beach is located on the southeastern North Carolina coast at latitude 34° North, longitude 77.5° West. Two test areas are located here; they are similar in environment, but very different in the severity of corrosion [1,2].

25-m Lot

The exposure area is 25-m from the ocean (mean tide). The test panels are positioned at 30° to the horizontal facing the surf in an easterly direction. The ocean waves and surf provide a continuous source of airborne salt particles (chloride ions) generating a severely corrosive environment (Fig. 2).

250-m Lot

The exposure area is 250 m from the ocean (mean tide). The test panels are positioned at 30° to the horizontal facing southward for maximum solar exposure. Airborne salt particles (chloride ions) carried by easterly wind generates a moderately corrosive environment (Fig. 3).

Evaluation and Interpretation

In an effort to determine the amount of corrosion occurring at three different marine sites, a test program was initiated in accordance with a new ASTM Recommended Practice Calibration of Atmospheric Test Sites (G 92). The results of a one year study revealed the severity of the



FIG. 1—Kure Beach marine atmospheric test sites 25 and 250 m from the ocean (aerial view looking west).



FIG. 2-Corrosion of wrought iron and chloride ion concentration in the 25-m lot.



FIG. 3-Corrosion of wrought iron and chloride ion concentration in the 250-m lot.

atmosphere in the 25-m lot compared to that in the 250-m lot and to a third a site at the LaQue Center's laboratories located on Banks Channel at Wrightsville Beach, NC (Table 1).

The evaluation and interpretation of atmospheric corrosion data involves measuring critical parameters of the test specimens, such as mass loss and corrosion rate, depth of attack, and visual appearance such as pitting or cracks in stressed samples. The evaluation tools will vary with the class of materials being considered. Steels are most readily compared by mass loss because of the relatively poor adherence of corrosion products. Other alloys can be evaluated by appearance because of a minimal mass loss resulting from surface reactions (pitting, oxide films, and so forth). Test specimens may be in the form of flat panels, stressed specimens, or various other forms simulating or duplicating actual product service.

Several environmental factors can influence the mechanisms of atmospheric corrosion [1,2]. These factors contribute to the uniqueness of a natural environment that has been compared to synthetic test environments [2]. In a marine atmosphere, the primary variables are the chloride content in the air, the time of wetness of a corrodible surface, and temperature. These variables are controlled by factors such as proximity to the ocean, elevation above sea level, prevailing winds, wave action, rainfall, humidity, and shelter [2,3].

Materials

As the first marine atmospheric corrosion test programs were being planned, the corrosion resistance of many metals and alloys needed to be documented. The corrosion test panels, nominally 10 by 15, 10 by 20 or 10 by 30 cm by 0.2 to 0.6 cm thick, were cut from flat plate materials. Materials among the first to be exposed at Kure Beach are identified in Table 2.

Several experimental and commercial aluminum alloys, identified in Table 3, were prepared for testing as U-bend stress corrosion specimens. Compositions of the experimental alloys were selected to provide magnesium contents ranging from 4 to 7% and also included manganese and chromium variations (Table 3). Several material tempers were included in the investigation (Tables 4 and 5): annealed (0 temper), strain hardened (H1), strain hardened and partially annealed (H2), and strain hardened and stabilized (H3). The final degree of strain hardening was also varied (as indicated by the second [H12] and third [H321] digits following the H1 [H12]. H2 [H22], or H3 [H321] designation). Also, specimens were either not aged, or were allowed to age naturally at room temperature for periods of one and three years, and in most cases quadruple specimens were evaluated in each temper. Commercial alloys 5456 (sensitized and not sensitized) and 5356 (sensitized) were also exposed with seven specimens of each temper and condition.

A group of materials consisting of high nickel alloys, stainless steels, high strength steels, a copper base alloy, and titanium alloys (Table 2) was prepared for exposure as two-point loaded bent beam stress corrosion specimens (ASTM Recommended Practice for Preparation and Use of Bent Beam Stress Corrosion Test Specimens [G 39]).

	LCCT K	ure Beach	LCCT Lab,
Materials	25-m Lot	250-m Lot	Banks Channel
Zinc ASTM B6	4	3.34	2.70
Steel ASTM A73	335	79.5	72.1
0.2% Copper Steel ASTM A-36	106	47.2	48.4

TABLE 1-Calibration of atmospheric test sites.

								Wei	ght, %						
Alloy	Condition	ïŻ	స	Fe	٩I	ä	cp	Mo	J	3	Cu	Mn	Si	Cb + Ta	Others
		ĺ			t c							07.0	00.0	0.07	
Inconer Alloy A-/Ju).	<u>כן</u> י	0.0	0.77	C.2	:	: .	cu.U	:	U.1J	0.40	00.0		:
Inconel ^a Alloy 718	annealed	68.9	18.6	ŝ	0.5	0.9	ŝ	3.1	0.04	÷	:	÷	:	:	:
Inconel" Alloy 600	:	80.7	12.9	5.8	÷	:	•	:	0.06	:	0.07	0.19	0.29	÷	:
Inconel ^a Alloy 625		61	21.5	2.5	0.2	0.2	:	9.0	0.05	÷	•	0.25	0.25	:	+ C0
Hastelloy ^h C	hot rolled	59	16	S	:	:	:	16	:	4	:	:	÷	:	:
Monel ⁴ Alloy 400	•	68	:	1.3	0.04	:	:	:	0.09	:	30	1.06	0.04	:	÷
Monel" Alloy K500	annealed	Bal	:		2.8	0.5	:	:	0.15	:	29.5	0.6	0.15	;	:
Incoloy" Alloy 800	•	32.5	21.0	46.0	0.38	0.38	:	:	0.05	:	0.38	0.75	0.5	:	+ C0
Incoloy" Alloy 825	:	42.0	21.5	30.0	0.10	0.90	÷	3.0	0.03	:	2.25	0.50	0.25	:	:
Nickel ⁴ Alloy 200		99.5	:	0.2	:	:	:	:	0.08	:	0.13	0.18	0.18	:	+ Co
Electrolytic nickel	:	99.5	:	:	:	:	:	:	:	:	:	:	:	:	:
Permanickel ^u allov 300		98.5	:	0.1	:	0.38	:	:	0.35	:	:	0.20	0.12	:	0.34 Mg
17-4 PH ⁶	:	4.0	16.5	Bal	:	:	:	:	:	:	•	:	:	0.3	:
AM 355 ^c		4.5	15.5	Bal				3.0			:	:	:	:	:
CD4MC _{II}		5	26	Ral				5.5		4.0				:	:
HVIDO		, c		n d				i							
4330	:	0.4	+ · · ·		:	:	:		:	. < : r	:	:			
4000	:	0.1	C0.U	Bal Bai	÷	:	• • •	C7.0		3.0	. u	:	:	:	:
Ni-Cu-Cb Steel	:	0.82	:	Bal	:	÷	0.09	:	0.04	÷	c.I	: ;		:	
9% Ni Steel	:	9.0	÷	Bal	÷	÷	:		0.10	:	:	0.50	0.27	:	: .
Stellite ^b	:	:	33	:	:	:	:	:	2.4	13	:	:	:	:	ol.6 Co
Ti alloy 6-4	:	:	÷	0.25	6.5	89.11	:	:	0.08	:	÷	:	÷	:	4.0 V,
Bervllium Conner	:							:		:	Bal	:	:	:	$N_2 + H_2$ 1.9 Be,
										•					0.25 Co
Everdur	:	:	:	0.06	:	:	:	:	:	:	95.90	1.10	3.10	:	:
70/30 CuNi	:	29.79	:	0.07	:	:	:	:	0.06	:	69.35	0.53	:	:	0.15 Zn
Constantan	:	44.78	:	0.09	, , ,	:	:	:	0.01	:	53.95	0.95	0.18	:	:
Nickel Silver	•	18.68	:	:	:	:	:	:	0.02	:	64.46	:	:	:	bal Zn
Ni-Resist," Type I		15.6	2.2	bal	:	÷	÷	:	2.9	:	6.6	1.3	2.3	:	:
Ni-Resist," Type III	•	28.9	2.8	bal	:	:	÷	:	2.5	:	:	0.5	1.7	:	:
Ductile, Type II	•	21.0	2.2	bal	:	:	:	:	2.8	:	:	1.1	2.3	÷	0.09 Mg
Ni-Resist," Type III	:	29.5	2.8	bal	:	:	:	:	2.4	:	:	0.6	2.3	:	0.10 Mg
"Trademark of the In	co Family of	f Compa	nies												
"Trademark of the Ca	bot Corpora	ation													
'I rademark of the Ar	mco Steel C	orporate	uc.												
"Trademark of the Al.	legheny Luc	llum Ste	el Corpo	ration											

TABLE 2-Nominal composition (essential elements).

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BAKER ON LONG-TERM CORROSION BEHAVIOR

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					Weight	., %			_
Alloy Number	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
		-	Exper	IMENTAL	Alloys				
32	0.10	0.09	0.00	0.00	3.87	0.00	0.02	0.02	balance
33	0.10	0.10	0.00	0.00	4.94	0.00	0.02	0.02	balance
34	0.09	0.09	0.00	0.00	5.96	0.00	0.03	0.02	balance
35	0.08	0.09	0.00	0.00	6.90	0.00	0.03	0.02	balance
36	0.10	0.13	0.00	0.67	4.17	0.14	0.01	0.02	balance
37	0.10	0.13	0.10	0.70	5.10	0.14	0.01	0.02	balance
38	0.10	0.12	0.00	0.79	5.96	0.12	0.01	0.02	balance
39	0.10	0.13	0.00	0.79	6.94	0.13	0.02	0.02	balance
			Соми	AERCIAL	Alloys				
5356		nom	inal com	position	94.6 Al.	0.12 Mn	. 5.0 Mg	0.12 Cr	
5456		non	ninal con	nposition	93.9 Al,	0.8 Mn,	5.1 Mg,	0.12 Cr	

TABLE 3—Chemical composition of experimental and commercial aluminum alloys.

	Condition in 198 Ratio: Numb	85 of U-Bend Samples er of Failures/Numbe	s in the 25-m Lot ^a or of Specimens
Temper	Not Aged	Aged 1 Year	Aged 3 Years
		G (ALLOY 32)	
0		0/4	0/3
H12	0/4	0/4	0/4
H16	0/4	0/4	0/4
H32	0/4	0/4	0/4
H36	0/4	0/4	0/4
	4% Mg, 0.67% Mi	n, 0.14% Cr (Alloy	36)
0	0/3	0/3	0/3
H12	0/3	0/4	0/4
H16	1/4	0/4	2/46
H32	0/3	0/4	0/4
H36	0/4	0/4	0/4
	5% Mc	S (Alloy 33)	
0	0/4	0/4	0/4
H12	1/4	0/4	0/4
H16	4/4	0/4	0/4
H32	0/1	0/4	1/4
H36	0/2	0/4	
	5% Mg, 0.7% Mn	1, 0.14% Cr (Alloy 3	37)
0	0/4	0/4	0/4
H12	4/4	4/4	4/4
H16	4/46	4/4	4/4
H32	2/3	0/4*	1/4
H36	0/4	0/4	0/4

 TABLE 4—Results of long-term atmospheric stress corrosion tests on experimental aluminum alloys (4 to 7% Mg).

	Condition in 198 Ratio: Numb	85 of U-Bend Samples er of Failures/Numbe	s in the 25-m Lot ^a r of Specimens
Temper	Not Aged	Aged 1 Year	Aged 3 Years
	6% Mc	G (ALLOY 34)	
0	1/4	0/4	0/4
H12	4/4	5/5	5/5
H16	3/3	4/4	3/3
H32	3/4	5/5	5/5
H36	2/2	4/4	3/4 ^b
	6% Mg, 0.8% Mr	I, 0.12% Cr (Alloy :	38)
0	0/3	0/4	0/4
H12	4/4	4/4	4/4
H16	4/4	4/4	4/4
H32	3/3	4/5	5/5
H36	0/4	0/4	0/4
	7% Mo	G (ALLOY 35)	
0	3/3	4/4	0/4
H12	5/5	5/5	5/5
H16	2/2	5/5	5/5
H32	5/5	5/5	5/5
H36	5/5	5/5	5/5
	7% Mg, 0.8% Mr	1, 0.13% Cr (Alloy)	39)
0	0/3	0/3	0/3
H12	4/4	4/4	5/5
H16		4/4	4/4
H32	0/3	0/4	0/4
H36	1/46	1/4 ^b	1/4 ^b

TABLE 4—Continued.

"Initial exposures were made in 1953. Test specimens remaining on test have 27-, 29-, and 30-year exposure.

^bExfoliation corrosion is evident on the samples remaining in the test.

Test Methods

The corrosion test panels were prepared for exposure and then exposed on test racks positioned at 30° to the horizontal facing south (ASTM Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens [G 1]). The panels were mounted in porcelain insulators that galvanically insulated each panel (ASTM Recommended Practice for Conducting Atmospheric Corrosion Test on Materials [G 50]). From these and other early exposures, evolved these and several other ASTM standard recommended practices.

The U-bend specimens used in these atmospheric tests were prepared from strips 178 by 19 by 1.6 mm. These strips were preformed to a 90° bend over a 13-mm radius and stressed by restraint in suitable test racks (ASTM Recommended Practice for Making and Using U-bend Stress Corrosion Specimens [G 30]). The test racks with experimental stressed specimens (not aged) were then placed on exposure in the marine atmospheric test lot, 25 m from the ocean (Fig. 4) in 1953. Additional test racks were added at later dates containing specimens aged at one and three years. Also, commercial alloy stressed specimens were exposed in 1957.

The two-point loaded bent beam stress corrosion specimens were cut to precise dimensions. The length was calculated so the amount of deflection would stress the specimens to 90% of the

	Ratio: Number of Failures/Number of Specimens			
	Not Sensitized		Sensitized ^b	
Alloy	Temper	Condition	Temper	Condition
5356			H321	0/7
5456	0	0/7	0	0/7
	H12	2/7	H12	7/7
	H16	2/7	H16	7/7
	H22	0/7	H22	0/7
	H24	0/7	H24	0/7
	H24	0/6	H24	0/7
	H24	0/6	H24	0/7
	H26	0/7	H24	1/7
	H32	0/7	H32	7/7
	H36	0/7	H36	7/7
	H321	0/7		
	H321	0/6	H321	0/5
	• • •	•••	H321	1/7

 TABLE 5--Results of long-term^a atmospheric stress corrosion tests of 5356 and 5456 aluminum alloys.

> Condition in 1985 of U-Bend Specimens Exposed in the 25-m Lot"

"Initially exposed in 1957, Alloy 5356 has been exposed for 24 years, Alloy 5456 has exposure periods of 24 to 27 years. "Sensitized (at 100°C for seven days to simulate long-term natural

^bSensitized (at 100°C for seven days to simulate long-term natural aging) before exposure.



FIG, 4-U-bend stress specimens exposed in the marine atmosphere 25 m from the ocean. The stressed specimens are mounted at 30° to the horizontal facing the ocean.

yield strength (ASTM G 39). Some specimens were cut from welded stock so that the weld ran the width of the specimen and was located in the center at a point that would have the greatest deflection. The specimens were then mounted in stress jigs and exposed in the 25-m marine atmospheric test lot as shown in Fig. 5.

Specimens designated for seawater test were exposed so only the deflected area of the specimen was immersed in low velocity seawater (0.5 m/s). After six-months' exposure, a selected number of these specimens were removed from seawater and re-exposed in the atmosphere simulating the intended use of the materials.

Plate specimens with circular welds were also exposed in the 25-m lot. The "restrained-weld" was prepared by drilling a hole in the center of the panels for automatic welding. A MIG weld was deposited in a circle 7.6 or 12.7 cm in diameter. Such a weld leaves high residual stresses in the plate, possibly equal to or exceeding the yield strength of the material (ASTM Recommended Practice for Preparation of Stress Corrosion Specimens for Weldment [G 58]).

Results

Corrosion Test Panels

Among the first test programs initiated in the marine atmosphere are a group of alloys that were exposed in the 250-m marine atmospheric lot on 14 May 1941. The materials included in this exposure are stainless steel Grades 2XX, 3XX, and 4XX, nickel silver, Everdur, 45/55 copper-nickel, 70/30 copper-nickel, Hastelloy C, and five nickel-base alloys. These continue on exposure and their appearance suggests varying degrees of corrosion resistance from good to excellent. The stainless steels display varying amounts of rust and rust stain on the panel surface



FIG. 5—Two-point loaded stress corrosion specimens exposed in the marine atmosphere 25-m from the ocean after 24-year exposure. The specimens were subjected to sandblasting when wind velocity was sufficient to blow sand from the beach.

depending on the alloy type, but generally the passive film provided good corrosion resistance. The copper-base alloys, copper-nickel alloys, and nickel-copper alloys generate a very adherent oxide film, which provided good corrosion resistance. The nickel-base alloys generate an oxide film, sometimes so thin it cannot be seen, which provides an excellent resistance to corrosion.

One test panel from each of five nickel-base alloys was evaluated after 36-year exposure, and the following results were obtained:

• Monel alloy 400—corrosion rate was 0.3 μ m/year, and the pit depth was 0.1 mm

• Monel alloy K500—corrosion rate was 0.2 μ m/year, and the pit depth was 0.2-mm maximum.

- Nickel alloy 200—corrosion rate was 0.25 μ m/year, and the pit depth was 0
- Permanickel alloy 300-corrosion rate was 0.2 µm/year, and the pit depth was 0

• Inconel alloy 600—corrosion rate was 0.008 μ m/year, and the pit depth was 0.1-mm maximum

The corrosion resistance of these and other nickel-base alloys is well documented in the literature [3,4].

Test panels of Hastelloy C and Stellite, prepared to a mirror polish, were exposed in the 250-m lot on 14 May 1942. Both materials continue on exposure and have a reflective mirror surface. These and other nickel-base alloys are identified in Table 6.

Marine Stress Corrosion Behavior of Al-Mg Alloys

After World War II, the most widely used aluminum alloy was 5154 (with nominal 3.5% magnesium) in ship structures [5]. This alloy was chosen because of good marine corrosion resistance, strength, and weldability. Strengthening of nonheat-treatable aluminum-magnesium alloys is achieved through cold working and strain hardening, although heating associated with welding decreases its strength. Early in the development of these alloys, the susceptibility to stress corrosion cracking of alloys containing more than 4.5% magnesium was recognized. However, it was conceivable that greater strength could be attained by a combination of composition and temper that would not be susceptible to stress corrosion cracking or excessive general corrosion.

Tests were initiated in 1953 to evaluate experimental aluminum-magnesium alloys with composition and temper variations, and commercial aluminum alloys 5456 and 5356. These tests

Material	Exposure Duration, years	Exposure Location (metres from ocean)
Monel Alloy 400	45	250
Monel Alloy K-500	45	250
Nickel Alloy 200	45	250
Permanickel Alloy 300	45	250
Inconel Alloy 600	44	250
Electrolytic Nickel	44	250
Hastelloy C	44	250
Stellite	44	250
Incoloy Alloy 800	28	25 and 250
Incoloy Alloy 825	28	25 and 250
Inconel Alloy X-750	26	25
Inconel Alloy 718	26	25
Inconel Alloy 625	21	25 and 250

TABLE 6—Some nickel base alloys exhibiting long-term marine atmospheric corrosion resistance (1 µm/year).

are continuing, and data that has been collected for more than 30 years are given in Tables 4 and 5.

Experimental Aluminum Alloys

4 Mg Binary Alloy—Fifty-three specimens were evaluated, and no failures occurred.

4 Mg-Mn-Cr Alloy—Fifty-six specimens were evaluated. The three failures occurred in the H-16 temper, one not aged (after 307 months) and two aged three years (112 and 190 months). The remaining nine specimens in the H-16 temper suffered severe exfoliation corrosion.

5 Mg Binary Alloy—Forty-seven specimens were evaluated with six failures. One failed in the H-12 temper, not aged (161 months), and one failed in the H-32 temper, aged three years (161 months). Four specimens failed in the H-16 temper, not aged (246-352 months). Severe exfoliation corrosion was observed on specimens in the H-16 temper.

5 Mg-Mn-Cr Alloy—Fifty-nine specimens were evaluated with 27 failures. All 12 failed in the H-12 temper (63-245 months), another 12 failed in the H-16 temper (94-362 months), and three failed in the H-32 temper, two not aged (17-250 months) and one aged three years (28 months). Severe exfoliation corrosion was observed on specimens in the H-16 temper, not aged and in the H-32 temper, aged three years.

6 Mg Binary Alloy—Sixty specimens were evaluated and 47 failed. All specimens failed in the H-12, H-16, H-32 and H-36 tempers. One specimen failure in the H-36 was attributed to exfoliation corrosion (Fig. 6). In addition, one annealed specimen failed after 211 months.

6 Mg-Mn-Cr Alloy—Sixty specimens were evaluated and 37 failed. All specimens failed in the H-12, H-16 and H-32 temper. Specimens not tempered or in the H-36 temper have not failed.

7 Mg Binary Alloy-Sixty-eight specimens were evaluated and all but the four specimens not tempered and aged three years have failed.

7 Mg-Mn-Cr Alloy—Fifty-three specimens were evaluated and 24 failed. All specimens in the H-12 and H-16 tempers failed. Three failed in the H-36 temper (one in each aging condition). The remaining nine show severe exfoliation corrosion. Annealed and H-32 tempered specimens have not failed.

Aluminum Alloy 5456

One hundred and sixty-two specimens were evaluated with 34 failures. Of the 81 nonsensitized specimens, only four failures occurred (two in the H-12 temper and two in the H-16 temper). At this time, the remaining seven specimens in the H-36 temper exhibit slight edge blistering and exfoliation corrosion (Table 5). Of the 81 sensitized (100°C/seven days) specimens, 30 failed, most in the H-12, H-16, H-32, and H-36 tempers after one month of exposure.

Aluminum Alloy 5356

Seven sensitized (100°C/seven day) specimens in the H-321 temper were evaluated, and no failures have occurred after 292-month exposure (Table 5).

Stainless Steels Corrosion Test Panels

Additional test results on the "Long-Term Atmospheric Behavior of Various Grades of Stainless Steel" have been described elsewhere in this symposium [6]. Results describe the performance of Types 2XX, 3XX, and 4XX grades of stainless steel, exposed in May 1958, after 26-year exposure in the 25- and 250-m lots at Kure Beach, NC. All the stainless steels tested exhibited a very good resistance to corrosion. However, all exhibited some degree of rust and rust staining. Insignificant pitting (<0.01 mm) was found on the boldly exposed flat surface of Types 2XX and 3XX grades. The most severe attack was found in a crevice area where two


FIG. 6—Failure of experimental aluminum alloy (6 Mg, binary, aged three years) after 322-month exposure in the 25-m lot caused by exfoliation corrosion (Top: tension side and bottom: edge exfoliation).

plates were overlapped and spot welded together. Additional long-term atmospheric corrosion results on stainless steels are documented in the literature [7-8].²

Stress Corrosion Resistance of Materials in Marine Atmospheres

Tests were initiated in 1961 to evaluate the stress corrosion resistance of various materials. The test specimens were in the form of two-point loaded bent beam stress corrosion test specimens and plate samples with circular welds, which were exposed in marine environments. Some of these stressed specimens and plate samples continue on test after 24-year exposure (Fig. 5).

Table 7 describes the materials exposed first in seawater, then re-exposed in the marine atmosphere. Table 8 describes the materials exposed only in the marine atmosphere. Table 9 describes the plate sample materials with a circular weld exposed in the marine atmosphere.

Some of the materials (duplicate specimens welded and not welded) exposed only in low velocity (0.5 m/s) seawater were removed from test without failure between 548- and 964-day

	Condition in 1985 of Two-Point Loaded Samples				
	Welded	Stress, ksi	Condition		
Inconel Alloy 718	no	133	OK		
Inconel Alloy 718	yes ^b	138	OK		
Inconel Alloy 718	vesc	118	OK		
Monel Alloy K-500	no	96	OK		
Monel Alloy K-500	ves	96	OK		
Hastelloy C	no	57	OK		
Hastellov C	ves	59	OK		
Hastelloy C Clad over HR 4330	ves	NR ^d	OK		
Beryllium Copper	no	110	OK		
Beryllium Copper	ves	110	OK		
17-4 PH (1025)	no	153	OK		
17-4 PH (1025)	ves	154	OK		
17-4 PH (1075)	no	157	OK		
17-4 PH (1075)	ves	160	OK		
C.P. Titanium Clad over HY-100	no	63	OK		
C.P. Titanium Clad over 4330	no	70	OK		
Titanium 821	no	N.R.	OK		
Titanium 6Al-4V	no	127	OK		
Titanium 6A1-4V	ves	127	OK		
CD4MCu	no	N.R.	OK		
AM-355	no	N.R.	OK		
HY-100	no	48	OK ^e		
4330	no	124	OK ^e		
4330	yes	124	OK ^e		
4330 (coated)	yes	171	OK ^e		

TABLE 7—Two-point loaded stress corrosion tests of alloys exposed for six months in seawater and then re-exposed in the marine atmosphere, 25-m from the ocean.

*Exposure time in 1985 is 24 years.

^bInconel Alloy 718 weld.

'Rene (trademark of ALLVAC Metals Co.) 41 weld.

^dNR-stress not recorded.

"Specimens were removed from test after 1403 to 1497-day exposure because of severe corrosion; no cracks were found.

exposure. These materials were Inconel Alloys 718, Monel Alloy K500, Hastelloy Alloy C, beryllium-copper, 17-4 PH stainless steel, CD4MCu cast stainless steel, titanium alloys 821 and 6-4, and HY100 steel. Failures did occur in the AM 355 cast stainless steel and 4330M steel.

Triplicate specimens of the materials originally exposed in low-velocity seawater (as listed above) were removed from seawater, after six-month exposure, and re-exposed in the 25-m marine atmospheric lot. Most of these materials have not failed after 24-year exposure. Specimens of HY100 and 4330M were removed from test between 1400- and 1500-day exposure because of severe corrosion.

Of the five welded specimens of each material exposed in the 25-m marine atmospheric lot, no failures have occurred in Inconel Alloy 718, 821 titanium, and 17-4 PH stainless steel. All HY100 specimens were removed because of severe corrosion. Of the thirty 4330M specimens, five longitudinally cut failed. The remaining 25 were removed from the test because of severe corrosion.

Plate samples with a circular weld, described in Table 9, have been exposed in the 25-m marine atmospheric lot for more than 22 years. Specimens of Inconel alloy 718, 17-4 PH stainless steel, 4330M steel, HY100 steel, and titanium 6Al-4V continue on exposure with no evidence of failure.

	Condition in 1985 of Two-Point Loaded Samples				
Alloys	Stress, ksi	Condition			
Inconel alloy 718	118	OK			
821 Titanium	110	OK			
17-4 PH (1025) (not coated)	154	OK			
17-4 PH (1025) (coated)	154	OK			
HY-100 (not coated)	105	OK¢			
HY-100 (coated)	105	OK¢			
4330 Transverse (not coated)	135	failure			
4330 (coated)	171	OK¢			
4330 Transverse	156	failure			
4330 Longitudinal	154	failure			
4330 Transverse ^b	156	OK			
4330 Longitudinal ^b	154	failure			

 TABLE 8—Long-term stress corrosion tests of alloys exposed to the marine atmosphere,

 25 m from the ocean.

"Exposure time in 1985 is 24 years.

^bSpecimens exposed in sealed polyethylene bags which were changed frequently due to moisture accumulation inside.

Specimens were removed from test due to severe corrosion; no cracks were found.

_	Condition in 1985 of Panels ^a						
	Dimension						
Alloys	Panel	Weld (Diameter)	Condition				
Titanium 6Al-4V	30 by 30 by 0.6	7.6	ОК				
Titanium 6Al-4V	30 by 30 by 0.6	12.7	OK				
Inconel Alloy 718	30 by 30 by 0.6	7.6	OK				
Inconel Alloy 718	30 by 30 by 0.6	12.7	OK				
17-4 PH (1025)	30 by 30 by 0.6	7.6	OK				
17-4 PH (1025)	30 by 30 by 0.6	12.7	OK				
17-4 PH (1025)	30 by 30 by 2.5	12.7	OK				
4330	30 by 30 by 0.6	7.6	OK				
4330	30 by 30 by 0.6	12.7	OK				
HY-100	20 by 20 by 0.6	7.6	OK				
HY-100	20 by 20 by 0.6	12.7	OK				
Titanium 8Al-2Cb-1Ta	30 by 30 by 1.25	7.6	failed ^b				

TABLE 9—Stress corrosion tests of alloys with a circular weld exposed in the marine atmosphere, 25 m from the ocean.

"Exposed 1962 to 1963.

^bFailure caused by stress corrosion cracking after 153-day exposure.

One titanium 8AI-2Cb-1Ta plate specimen cracked after 153-day exposure in the 25-m lot. The specimen measured 30 by 30 by 1.25 cm with a 7.6-cm-diameter weld. Two saw cuts were made to open the fracture for study. Replicas of the fracture were made for observation in the electron microscope. They showed the "river patterns" and other characteristics typical of a cleavage type of failure. Specimens were cut from one edge of the plate outside the weld-heat-affected zone for stress corrosion tests using the precracked cantilever beam method with $3^{1}/2\%$ sodium chloride (NaCl) solution as the corrodent. Stress corrosion crack propagation

was observed (K_{1SCC}) at 32 ksi \cdot in.^{1/2}. The torque required to break a dry specimen was 99 ksi \cdot in.^{1/2} [9].

Examination of the stress corrosion specimen revealed the stress corrosion fracture was cleavage, whereas the fast fracture was dimpled rupture. It was concluded that the crack in the welded plate propagated by stress corrosion cracking, and not as a purely mechanical cracking. Also, the drilled hole in the center of the plate was sufficient to provide the required stress intensification [9].

Steels and Copper Test for Corrosion Resistance in Accordance with ASTM G 50 Corrosion of Metals and Alloys in Marine Atmospheres

Since steel is a primary structural material used in many designs, its corrosion behavior is an extremely important factor. The behavior to a great extent is controlled by alloying agents such as nickel (Fig. 7), chromium (Fig. 8), and copper (Fig. 9). Steels also have been alloyed for specific functions such as high strength, low alloy nickel-copper-columbium steel, ASTM A710 (Fig. 10) and 9% nickel steel for pressure vessels, ASTM A353 (Fig. 11). The marine atmospheric corrosion resistance of cast iron, ductile iron, Ni-Resist[®], and ductile Ni-Resist[®] have been examined, and results are shown in Fig. 12. The literature contains further information on the corrosion of low alloy steels [10, 11].

A test was initiated in marine atmospheres to determine if the corrosion resistance of copper should be significantly affected if exposed boldly, or under a shelter. The results revealed that greater attack occurs in a sheltered exposure where contaminates gather and stay, than in a bold exposure where contaminates are washed from the surface by rain (Fig. 13). The long-term corrosion resistance of copper and copper-base alloys is well documented in the literature [12-15]. The corrosion resistance is attributed to the formation of a very adherent oxide film that forms a protective barrier on the surface of these materials.



FIG. 7-The effect of nickel content on atmospheric corrosion behavior of steel.



FIG. 8—The effect of chromium content on atmospheric corrosion behavior of steels.



FIG. 9-Corrosion of alloy steel and copper steel in marine atmospheres.



FIG. 10-Corrosion of Ni-Cu-Cb steel in marine atmospheres.



FIG. 11-Corrosion of 9% nickel steel exposed in the marine atmosphere.



FIG. 12—Corrosion of cast iron, ductile iron, Ni-Resist and ductile Ni-Resist after 15 years in marine atmospheres.



FIG. 13-Corrosion of copper in marine atmospheres bold and sheltered exposures.

Conclusions

An evaluation of the corrosion performance of materials in natural marine atmospheres is essential. Understanding the many factors that influence this corrosion is also essential.

The atmospheric corrosion resistance of nickel-base alloys stems from the formation of a very thin oxide film that renders the alloys virtually immune to corrosion over many years of exposure.

An aluminum-4% magnesium alloy exhibited excellent resistance to stress corrosion failure. Increasing magnesium levels resulted in increasing failure rates, alloying with manganese and chromium appears beneficial, but SCC resistance depends upon temper. The commercial 5356 has excellent resistance to stress corrosion cracking even when sensitized. Alloy 5456 performed well, but stress corrosion failures did occur at some tempers. Sensitizing increased the failure rate.

Many 2XX and 3XX grades of stainless steel provide a good resistance to marine corrosion. Most grades of stainless steel do exhibit varying degrees of rust staining or rust scale in moderate and severe marine environments; therefore, manufacturers have provided simple cleaning methods. Attack in crevices is usually greater than on the bold surfaces.

A number of alloys continue to resist stress corrosion cracking after 24 years of exposure. The materials include Inconel Alloy 718, Monel Alloy K-500, Hastelloy Alloy C, beryllium copper, 17-4 PH stainless steel, AM 355 stainless steel, CD4MCu stainless steel, and titanium 6AI-4V alloy. High strength steels, 4330M and HY100, are susceptible to corrosion and stress corrosion failure in the marine atmosphere.

The general corrosion resistance of steel is greatly improved with the addition of chromium, copper, or nickel. Copper has a very good resistance to corrosion; however, corrosion is accelerated when it is under a shelter where contaminate buildup with chlorides present can produce active corrosion sites on the metal surface at times of high humidity.

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Atmospheric Corrosion Behavior of Clad Metals

REFERENCE: Haynes, G. and Baboian, R. "Atmospheric Corrosion Behavior of Clad Metals," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 145-190.

ABSTRACT: Atmospheric corrosion of clad metals has been studied by direct exposure at nine tests sites throughout the United States. Qualitative and quantitative results are presented for a wide range of clad metal combinations for copper, nickel, aluminum, and several of their alloys, and also stainless steels. Included are results of five exposure periods including the final exposure period of 15 years.

KEY WORDS: atmospheric corrosion, clad metals, galvanic corrosion, copper, copper alloys, steels, stainless steel, stainless steel-clad aluminum, steel substrates, copper-clad stainless steels, copper-clad aluminum, galvanic couple, localized corrosion, corrosion rate.

Clad metals are metallurgical materials systems that are part of a large group of materials termed composites [1]. They consist of two or more metals or alloys which are metallurgically bonded to provide properties that are not available in a single material. The unique properties of clad metals as well as the need for conservation of critical materials has resulted in wide-spread use of clad metals. They are currently used for a wide range of applications, such as coinage materials, structural materials, electronic materials and materials for the communications and transportation industries.

This diversity of applications has led to the exposure of clad metals to a wide range of natural environments. Since they are composed of dissimilar metals, galvanic corrosion can occur. Because of the unique construction of clad metals, their corrosion behavior may be different than multimetal systems produced by other techniques. For example, the corrosion performance and design parameters for clad metals has been compared by Baboian to those of electrodeposited coatings [2].

This test program determines the atmospheric corrosion performance of a wide range of clad metal systems in various natural environments. Results for copper clad stainless steels after exposure for 7.5 years have been reported previously [3]. This paper reports the results for 39 materials which were exposed at nine atmospheric test sites for 15 years. Data is given for five exposure periods, including the final exposure period of 15 years.

Experimental Procedure

The materials that were exposed at the nine atmospheric test sites (Table 1) are listed in Table 2. The test sites included rural, urban industrial, and marine environments. Three of the test sites were ASTM exposure sites.

¹Member of technical staff and head, respectively, Texas Instruments Inc., Electrochemical and Corrosion Laboratory, Attleboro, MA 02703.

Туре
rural
urban industrial
urban industrial
rural
marine
marine
industrial (ASTM site)
marine (ASTM site)
marine (ASTM site)

 TABLE 1—Atmospheric exposure test sites.

Material	Thickness (Inches)	Cladding Ratio (Percent)
1006 steel	0.033	
corten	0.034	
type 409 stainless steel	0.050	
type 430 stainless steel	0.034	
type 321 stainless steel	0.015	
ofhc copper	0.032	
85-15 brass	0.029	• • •
70-30 brass	0.020	
commercial bronze	0.031	
nickel	0.032	
1100 aluminum	0.037	
3003 aluminum	0.036	
5052 aluminum	0.050	•••
cu/1006 steel/cu	0.015	10/80/10
bronze/1006 steel/bronze	0.050	10/80/10
ni/1006 steel/ni	0.053	10/80/10
85-15 brass/1006 steel/85-15 brass	0.025	20/60/20
cu/corten/cu	0.015	10/80/10
cu/corten/cu	0.030	10/80/10
85-15 brass/corten/85-15 brass	0.015	10/80/10
bronze/corten/bronze	0.015	10/80/10
cu/409 stainless steel/cu	0.015	10/80/10
cu/409 stainless steel/cu	0.030	10/80/10
cu/409 stainless steel/cu (scribed)	0.030	10/80/10
85-15 brass/409 stainless steel/85-15 brass	0.015	10/80/10
bronze/409 stainless steel/bronze	0.015	10/80/10
cu/430 stainless steel/cu	0.032	10/80/10
cu/321 stainless steel/cu	0.035	15/70/15
434 stainless steel/3003 aluminum	0.025	20/80
434 stainless steel/5052 aluminum	0.026	20/80
304 stainless steel/3003 aluminum	0.024	20/80
201 stainless steel/3003 aluminum	0.024	20/80
304 ss/7072 al/3004 al/7072 al/304 ss	0.076	20/5/50/5/20
cu/1100 aluminum	0.022	20/80
cu/1100 aluminum/cu	0.031	10/80/10
cu/3003 aluminum/cu	0.020	10/80/10
cu/5052 aluminum	0.020	20/80
cu/5052 aluminum/cu	0.020	10/80/10
lead/cu/5052 aluminum/cu/lead	0.021	2.7/7.5/80/7.5/2.5

TABLE 2-List of materials in atmospheric exposure program.

The atmospheric test panels were prepared and exposed according to ASTM G 50, Standard Practice for Conducting Atmospheric Corrosion Tests on Metals. Before exposure, the panels were cleaned using the techniques described in ASTM G 1 on Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens. The recommended chemical cleaning solutions were chosen so that they did not attack either the cladding or the substrate. When this was not possible, the specimens were mechanically cleaned. The 100 \times 150-mm (4 inch \times 6 inch) test panels were coded and marked by stamping. The thickness was measured to the nearest 0.01 mm (0.001 in.) and the length and width were measured to the nearest 1 mm (0.1 in.). The mass was measured to the nearest 0.01 g.

The test panels were exposed at various times during 1967. Duplicate panels of single clad materials were exposed for each exposure period so that both sides were exposed facing skyward. In some cases more than one thickness of a particular clad combination was exposed.

A single test panel was retrieved from each test site after 0.5, 1.5, 3.5, 7.5, and 15-years' exposure. However, all test panels were retrieved from Houston and from Anaheim after the 7.5-year exposure period. After exposure, each panel was examined visually, photographed, and rated for degree and type of corrosion using the six digit rating system in Table 3. The first two digits (A and B) evaluate the extent of corrosion of the surface of the panels, while the last four digits (C, D, E, and F) rate the extent of galvanic corrosion at pores and exposed edges. The rating for galvanic pitting (C) indicates the degree of galvanic corrosion of the substrate at pores or damages in the clad surface (including the identification stamps). The rating for tunneling (E) indicates the maximum distance of localized corrosion and is shown in Fig. 1 for copper clad 430 stainless steel with the copper cladding removed to show the substrate and in Fig. 2 for copper clad 5052 aluminum. The rating for delamination (F) indicates the distance of complete delamination of the cladding from the edge caused by corrosion of the substrate. An



FIG. 1—Copper/430 Stainless Steel/Copper after 1.5 years' exposure showing galvanic tunneling (copper cladding has been partially removed to show stainless steel substrate).

test panels.
atmospheric
evaluation of
system for
TABLE 3-Rating

				Rati	ings		
	Type of Corrosion	0		2	3	4	5
Bulk surface	(A) uniform	none	slight four challour	moderate	heavy	very heavy	destruction
	ammid (a)		pits	many snanow pits	new ueep pits	niany ucep pits	restruction
Degree of galvanic attack at edges	(C) galvanic pitting	none	at identification stamp	1 to 2	3 to 5	6 to 20	destruction
and pores	(D) edge corrosion	none	slight	moderate	heavy	very heavy	destruction
	(E) tunneling	none	1/16 in."	1/4 in."	1/2 in.ª	1 in."	3 in."
	(F) delamination	none	1/16 in."	1/4 in."	1/2 in."	1 in."	3 in."

"1 in. = 2.54 cm.



FIG. 2—Copper/5052 Aluminum/Copper after 1.5 years' exposure showing galvanic tunneling (Ratings are in Table 4).

example of the use of the rating system is shown in Table 4, which lists the corrosion ratings of the specimens in Figure 2. After visual evaluation, the test panels were first scrubbed with a nylon bristle brush to remove loosely adhering corrosion product and then cleaned according to ASTM G 1 and weighed. Mass changes were obtained for all of the materials after each exposure period.

Results and Discussion

Mass losses and corrosion ratings are tabulated in Appendix A in Tables A1a through A39b. It is important to note that for some materials the mass losses (Table a) were often misleading or inconsequential. In these cases the corrosion rating system (Table b) provided a valuable tool

	Rating					
Site	A	В	С	D	Е	F
Houston	1	0	1	3	2	2
Miami (inland)	1	0	1	2	2	1
Miami (coastal)	1	0	1	2	2	1
Newark	1	0	0	2	1	0
Kure Beach (800 ft)	1	0	1	2	3	2
Kure Beach (80 ft)	1	Ō	2	3	3	3

 TABLE 4—Corrosion ratings for copper/5052 aluminum/copper

 after 1.5 years' exposure (see Fig. 2).

for conveying the true condition of the specimens in a compact comprehensible form. For comparative purposes all data are reported as total mass loss (or gain) for a four in. by six in. test specimen. This was necessary since galvanic effects for some clad combinations made the calculation of corrosion rates (i.e., in mils per year) impossible.

Steels and Stainless Steels

The data for 1006 steel (Tables A1a and A1b) gives an indication of the relative corrosivity of the test sites [4]. Although Attleboro was considered to be a rural site because of the lack of heavy industry in the immediate area, the mass loss data indicate that it is more properly classified as an industrial site since the mass losses and corrosion ratings were similar to those of Newark. The 1006 steel specimens at the Kure Beach 240-m lot were virtually destroyed after the 3.5-year exposure period (Table A1b), indicating that this was an extremely corrosive site. The Miami sites, although classified as marine sites, had an intermediate range of mass losses for the 1006 steel. This was probably because the coastal site was located on the roof of a highrise building approximately 0.4 Km or one quarter mile from the ocean, while the inland site was several miles from the ocean. The Dallas and Houston sites were correctly categorized as urban industrial sites since they had lower mass losses than the industrial site (Newark) and higher mass losses than the rural site (Anaheim).

Improved corrosion resistance for CORTEN weathering steel (Tables A2a and A2b) was evident at all of the test sites [5]. After the 3.5-year exposure period, its mass loss was one half that of 1006 steel at Newark and one third that of 1006 steel at Kure Beach (240-m lot). Unfortunately the test specimens for the longer exposure periods were lost. Based upon the data for the 1006 steel and CORTEN, the relative corrosivity of the atmospheric test sites in this program was:

Kure Beach (24-m) > Kure Beach (240-m) > Newark > Attleboro > Houston

> Miami (coastal) = Miami (inland) > Dallas > Anaheim

The mass loss data for Type 409SS (Table A3a), Type 430SS (Table A4a), and Type 321SS showed no differentiation among these alloys except that Type 409SS had a significantly higher mass loss of 0.40 g after 15 years' exposure at Kure Beach (24 m). As indicated by the ratings (Tables A3b, A4b, and A5b), superficial pitting and rusting occurred on all of these alloys, with the degree of rusting decreasing in the order: 409SS to 430SS to 321SS. The 409SS pitted earlier than Type 430SS, while Type 321SS took the longest to show signs of pitting and red rust.

Copper and Copper Alloys

The mass losses for oxygen free copper (Table A6a) were converted to the penetration rates, which are listed in Table 5. As expected, the average corrosion rate in terms of mils per year at the end of an exposure period decreased with increased exposure time due to the formation of a protective patina [6 to 10]. The average corrosion rate stabilized after 7.5 years in Attleboro, Dallas, Miami (inland), and Newark since the rates for the 7.5-year and 15.0-year exposure periods were nearly identical. The average corrosion rate in Miami (coastal) and Kure Beach (24- and 240-m lots) was less after 15.0 years than after 7.5 years, indicating that the corrosion rate had not stabilized. This suggests that the chloride ion plays an important role in the nature of the patina formed on copper. These observations correlate well with the color of the patina, which is noted in Table A6b. At those sites where the corrosion rate was stable, a green patina had formed, while at those sites where the corrosion rate had not stabilized, the patina was either black or brown. Thus, in the same environment, the green patina formed on copper appears to be more protective than the intermediate black or brown patina.

Site	0.5 Years, mils/year"	1.5 Years, mils/year ^a	3.5 Years, mils/year ^a	7.5 Years, mils/year ^a	15.0 Years, mils/year ^a
Attleboro	0.047	0.047	0.041	0.030	0.029
Dallas	0.062	0.01	0.038	0.020	0.017
Houston	0.062		0.038		
Anaheim		0.031	0.020	0.014	
Miami (inland)	0.062	0.02	0.027	0.015	0.012
Miami (coastal)			0.074	0.048	0.034
Newark	• • •	0.057	0.063	0.040	0.038
Kure Beach, 24-m (80-ft) lot	0.250	0.114	0.114	0.062	0.033
Kure Beach 245-m (800-ft) lot	0.250	0.114	0.092	0.062	0.035

TABLE 5—Corrosion rate of copper.

 $^{\circ}1 \text{ mil} = 25.4 \text{ m}.$

Corrosion ratings and mass losses for commercial bronze, (90-10 brass), 85-15 brass, and 70-30 brass are listed in Tables A7, A8, and A9 respectively. Uniform corrosion of the brasses occurred as indicated by the ratings. The brasses went through the same color changes as copper except that, as shown in the rating tables, they tended to require more time to form the green patina. The mass loss data for the 15-year exposure period is converted to penetration rates in Table 6. As the zinc content of the alloy increased, the corrosion rate tended to decrease in marine environments (Kure Beach and Miami coastal) and to increase in industrial environments (Newark and Attleboro) [11]. The corrosion rates of copper and copper zinc alloys (brasses) were similar in rural and urban-industrial environments.

Nickel

The mass losses and corrosion ratings for nickel are in Tables A10a and A10b. Mass losses were low and uniform over time. The test panels assumed a brown matte surface appearance at all of the test sites. Highest mass losses were measured in industrial environments.

	Corrosion Rate (mils per year)						
Location	Of Copper	Commercial Bronze (90 Cu-10 Zn)	85-15 Brass	70-30 Brass			
Attleboro	0.029	0.031	•	0.040			
Dallas	0.017	0.018	0.018	0.016			
Houston ^e	•••	0.033	0.042	0.041			
Anaheim"	0.014	0.014	0.016	0.020			
Miami (inland)	0.012	0.013	0.016	0.013			
Miami (coastal)	0.034	0.018	0.018	0.014			
Newark	0.038	0.046	0.050	0.055			
Kure Beach (80-ft)	0.033	0.029	0.031	0.021			
Kure Beach (800-ft)	0.035	0.031		0.023			

TABLE 6-Corrosion Rate data for 15-year exposure of copper and copper alloys.

"7.5-year exposure.

Aluminum

The aluminum alloys had superficial pitting and general corrosion. Mass changes and corrosion ratings for 1100 aluminum, 3003 aluminum, and 5052 aluminum are in Tables A11, A12, and A13. Since the alloys were not anodized prior to exposure, the mass gains as well as the mass losses were influenced by the formation of a thin adherent oxide upon exposure. The 3003 and 5052 aluminum had larger mass losses after 15 years than the 1100 aluminum (mass gain). However, as indicated by the ratings, the visual appearance of all aluminum alloys was similar. The surface of the specimens was grainy grey at all of the sites except the industrial sites (Newark and Attleboro), where a grainy brown surface was formed.

Steel Substrates

Galvanic corrosion of the steel substrate was substantial on all clad steel combination. The mass losses for copper-clad steel (Table A14a) were much greater than for solid copper (Table A6a) after 15 years, indicating that galvanic corrosion of the steel substrate was substantial. With the exception of Newark, the galvanic effect of the steel on the copper surfaces was restricted to about 12.7 mm (1/2 in.) from the exposed edge after 15 years as shown in Fig. 3. The area not affected by the steel had a patina similar to that of solid copper at each site. The test specimens in Attleboro and Kure Beach (24-m) were destroyed by corrosion after 15 years. As the ratings show (Table A14b), edge effects became visually significant after 3.5 years of exposure. Edge corrosion was very heavy after 15 years with tunneling and delamination up to 25.4 mm (1 in.) from the edges. These results are not surprising since the steel was only exposed at the cut edge of the 0.38-mm (0.015-in.) thick specimen, resulting in a very high cathode (copper) to anode (steel) area ratio.

The galvanic effect between 85-15 brass and the steel substrate was not as severe as that of copper. After 15 years of exposure, the specimens (Fig. 4) had a green or brown matte surface similar to solid 85-15 brass except for a rust stained zone $6.35 \text{ mm} (^{1}/_{4} \text{ in.})$ in from the edges. Tunneling and delamination were $6.35 \text{ mm} (^{1}/_{4} \text{ in.})$ deep after 15 years. Although mass losses for 85-15 brass clad steel (Table A16a) were similar to those of 85-15 brass (Table A8a), the



FIG. 3—Copper/1006 Steel/Copper after 15 years' exposure showing the degree of galvanic effect at edges.



FIG. 4-85-15 Brass/1006 Steel/85-15 Brass after 15 years' exposure showing magnitude of galvanic effects.

ratings (Table A16b) indicate that direct comparisons cannot be made, since edge corrosion was heavy and there was a possibility of entrapped corrosion product from the tunneling. The mass gains after 3.5 years exposure in Miami and Kure Beach show that the effect of entrapped corrosion products can be significant. The difference in the degree of corrosion of the 85-15 brass-clad steel and copper-clad steel can be attributed either to brass being a less effective cathode or a difference in area ratio since the 85-15 brass clad steel (0.56 mm or 0.022 in.) was twice as thick as the copper clad steel.

Nickel-clad steel (1.35 mm or 0.053 in.) after 15 years of exposure is shown in Fig. 5. It had the same brown matte surface as solid nickel except for a narrow zone at the edges. The ratings



FIG. 5-Appearance of Nickel/1006 Steel/Nickel after 15 years' exposure.

(Table A17b) show that very little tunneling or delamination occurred throughout the test program, although after 15 years of exposure, edge corrosion was heavy. The mass changes for nickel-clad steel (Table A17a) were slightly greater than those for solid nickel (Table A10a), reflecting the edge corrosion that occurred. In this case, comparison between the nickel-clad steel and solid nickel data is valid because the rating table shows no interfering effects such as galvanic pitting or tunneling. The nickel-clad steel had the best performance of all of the steel substrate combinations. Whether this is due to a difference in the cathodic efficiency of the nickel cladding or an area ratio effect is not clear.

Corrosion ratings and mass changes for materials with CORTEN substrates are listed in Table A18a through A21b. The rating tables for all of these materials show that galvanic tunneling and galvanic pitting were substantial problems after only 3.5 years of exposure. The severity of these corrosion mechanisms increased with continued exposure. The mass change data were widely scattered with large mass gains from entrapped corrosion products in many cases. Based on the corrosion ratings, no discernible differences in corrosion behavior was found for copperclad CORTEN (Table A18b), commercial bronze-clad CORTEN (Table A21b), and 85-15 brass-clad CORTEN (Table A20b) when comparing equal thicknesses (0.015 in.). The corrosion ratings for 0.76 mm (0.030 in.) copper clad CORTEN (Table A19b) show that increasing the substrate thickness (and thus decreasing the cathode to anode area ratio) did result in somewhat better resistance to tunneling and delamination than the 0.38 mm (0.015 in.) copper-clad CORTEN (Table A18b). This effect was more pronounced after the 3.5-year and 7.5-year exposure periods at all sites except Kure Beach. Comparison of the ratings for equal thicknesses of copper-clad steel (Table A14b) and copper-clad CORTEN (Table A18b) shows that there was no beneficial effect of a weathering steel (CORTEN) as a substrate. Thus, the galvanic couple with copper overrides the beneficial aspects of the weathering steel.

Copper Clad Stainless Steels

The mass change data and corrosion ratings for copper clad stainless steels are in Tables A22a through A28b. The stainless steel substrates were either Type 409, Type 430, or Type 321. As indicated in the rating tables, corrosion of the stainless steel substrates was highly localized, with the predominant mechanism of corrosion being tunneling. The visual appearance of the copper surface of the copper-clad stainless steels was identical to that of monolithic copper, except at those sites where the corrosion of the substrate was severe, causing rust staining (rating of three or more for edge corrosion).

Since galvanically induced localized corrosion of the substrates did occur, mass changes can be misleading and should only be evaluated in conjunction with the rating system. For example, the mass loss for copper clad Type 409 at Kure Beach (240-m) after 7.5 years (Table A23a) was only one-third the mass loss for monolithic copper (Table A6a). However, as indicated by the 201330 rating, this reduction in mass loss was due to the entrapped corrosion product and does not, therefore, represent a lower overall corrosion rate. On the other hand, the mass losses for copper-clad Type 321 (Table A28a) can be converted to penetration rates since the rating Table (A28b) indicates that no corrosion of the substrate occurred. Note that the mass losses for this combination are similar to those of monolithic copper (Table A6a) in all environments.

The observed type of corrosion was a function of either the environment and the stainless steel substrate or both, and was independent of the copper alloy. In rural and industrial environments, all of the copper-clad stainless steels had uniform corrosion of the copper surfaces with no localized corrosion of the substrates. In chloride containing environments (Miami and Kure Beach as well as Dallas, which contained chlorides resulting from industrial pollution), galvanically induced localized corrosion of the substrate occurred in copper-clad Types 409 and 430 (Tables A22b, A23b, A24b, and A27b). Identical results were obtained for commercial bronze (90 Cu-10 Zn) clad Type 409 (Table A26b) and 85-15 brass-clad Type 409 (Table A25b), indicating that the composition of the copper alloy cladding had little or no effect on localized

corrosion of the substrate. The importance of the chloride ion on this phenomena is demonstrated in Fig. 6, which shows the test specimens after 15 years' exposure at Kure Beach and Newark. In addition to tunneling from the exposed edge, localized corrosion of the stainless steel substrate occurred along the scribe lines where the substrate was exposed. The 310100 rating at Newark, 313221 rating at Kure Beach (240-m), and 313332 rating at Kure Beach (24-m) in Table A24b accurately reflect the condition of these specimens. In contrast to the results for copper-clad steel, the thickness of the copper clad-stainless steel had little effect on corrosion of the substrate (Tables A22b and A23b).

Stainless Steel Clad Aluminum

With the exception of Type 304 stainless steel/7072 aluminum/3004 aluminum/7072 aluminum/Type 304 stainless steel, all of the stainless steel-clad aluminums were single-clad materials. Specimens of each were exposed with the aluminum facing skyward and with the stainless steel facing skyward. Ratings for the bulk surface (first two digits) are for the skyward facing surface.

Mass changes and corrosion ratings are included in Tables A29a through A33b. With few exceptions, mass changes were quite small and the corrosion ratings provided the most significant data.

The ratings for the bulk surface (first two digits) of the 434SS/3003 aluminum with the aluminum facing skyward (Table A29b) were similar to those for monolithic 3003 aluminum (Table A12b) for all of the exposure periods. In this orientation, the galvanic effect with the 434SS was small, as shown by the moderate ratings for edge corrosion and the absence of tunneling and delamination. The ratings for the specimens with the 434SS facing skyward (Table A29d) show no or slight pitting during the 15-year exposure period. The ratings for galvanic effects



FIG. 6—Copper/409 Stainless Steel/Copper after 15 years' exposure showing localized corrosion of the substrate in chloride containing environments (Kure Beach) and no localized corrosion in industrial environments (Newark).

(fourth through sixth digits) again show small galvanic effects except for the 7.5- and 15-year exposure periods at the Kure Beach 240-m lot, which indicate severe tunneling. The reason for this behavior is unclear, since tunneling of this combination did not occur at the other marine sites. The lack of galvanic effects for 434SS clad 3003 aluminum is not surprising, since stainless steels are easily polarized and the cathode to anode area ratio is one for single clad systems.

Tunneling and delamination were more severe for 434SS clad 5052 aluminum than for 434SS and 3003 aluminum at both Kure Beach sites. The ratings for 434SS clad 5052 aluminum (Tables A30b clad A30d) show that from 1.6 to 25.4 mm (one-sixteenth to one in.) of tunneling and delamination occurred after the longer exposure periods. This effect could be related to the composition of the aluminum and the metallurgy of the bond, since brittle, active intermetallic compounds are possible in the stainless steel-aluminum system. Results at all of the other test sites were similar for both stainless steel clad aluminums, with little or no significant galvanic effects.

Results for 304SS-clad 3003 aluminum (Table A31) and 201SS-clad 3003 aluminum (Table A32) were also similar. Mass changes were small or nonexistent irrespective of specimen orientation. With the aluminum surface facing skyward, the aluminum surface became grainy grey except at industrial sites, where it became grainy brown. With the stainless steel surface facing skyward, a few shallow pits were observed after 7.5 or 15 years' of exposure. There was no noteworthy difference between the stainless steels. The ratings for edge corrosion were identical to those for the bulk surface, indicating little or no significant galvanic effect. This was reinforced by the absence of tunneling and delamination.

The performance of 304SS/7072 aluminum/3004 aluminum/7072 aluminum/304SS (20/5/50/5/20) (Table A33) contrasted sharply with that of single clad stainless steel clad aluminums. This combination obviously had a much higher cathode (304SS) to anode (aluminum) area ratio. After 3.5 years' exposure, edge corrosion was moderate in Attleboro and Kure Beach (both sites) with up to 12.7 mm (one-half in.) of tunneling and delamination. After 15 years' of exposure, up to 76.2 mm (three in.) of delamination had occurred at these sites. Corrosion appeared to be restricted to the relatively thin 7072 aluminum thicknesses. It appears that the 7072 aluminum was either more active than the 3004 aluminum or formed a very active intermetallic compound. In either case, corrosion was localized at the 304SS-7072 aluminum bond line, resulting in rapid delamination.

Copper Clad Aluminum

All of the copper clad aluminum combinations (Tables A34a to A39b) were very susceptible to galvanic effects. The mass loss data for single-sided copper-clad 1100 aluminum (Table A34a) showed a trend that was consistent for all of the copper-clad aluminums. Mass losses increased during the 0.5- and 1.5-year exposure periods as galvanic corrosion at the edge was initiated, although the mass losses were less than those of monolithic copper (Table A6a). As tunneling proceeded and corrosion products became entrapped, mass gains were measured (3.5 years' exposure). For the 7.5- and 15-year exposure periods, delamination of the cladding facilitated removal of the corrosion product and large mass losses were measured. Another phenomena which was more prevalent with copper clad aluminums was galvanic pitting (the third digit in the rating code). As shown in Figure 7, this occurs at pores or damage sites in the more noble copper cladding. The small surface area of aluminum exposed results in a very high cathode to anode area ratio. This leads to rapid galvanic corrosion and, where corrosion products remain trapped, bulging of the cladding.

The ratings for single sided copper clad 1100 aluminum show that the magnitude of corrosion was not affected by whether the aluminum (Table A34b) or copper (Table A34d) was facing skyward. With the exception of the industrial sites (Attleboro and Newark), tunneling and delamination were between 6.35 to 25.4 mm (one-quarter and one in.) after 3.5 years exposure,



FIG. 7-Galvanic pitting at pores and damage sites on Copper/Aluminum/Copper.

with the marine sites having the greater effect. After 15 years' exposure, complete delamination had occurred at most of the sites as indicated by the five ratings for delamination (Fig. 8).

The data for double-sided copper-clad 1100 aluminum (Table A35) shows that the cathode (copper) to anode (aluminum) area ratio influenced the rate of delamination. The ratings for tunneling and delamination were one or two rating levels worse at all of the sites after equivalent exposure periods. The unfavorable area ratio resulted in ratings of four to five for tunneling and delamination after only 3.5 years' exposure. As shown in Fig. 9, the specimens were essentially retrieved in three pieces after 15 years' exposure. The data for double-sided copper-clad 3003 aluminum shows that this combination was not as bad as double-sided copper-clad 1100 aluminum, although corrosion was still very severe.



FIG. 8-Delamination of Copper/1100 Aluminum after 15 years' exposure.



FIG. 9-Copper/1100 Aluminum/Copper after 15 years' exposure showing degree of delamination.

Although galvanic corrosion of both single and double sided copper clad 5052 aluminum was severe, it was less severe than copper-clad 1100 aluminum. The rating tables show that the single-sided material (Tables A37b and A37d) did not completely delaminate after 15 years' exposure, although up to 25.4 mm (one in.) of delamination was measured in the more aggressive sites. The double-clad material (Table A38b) was essentially destroyed after 15 years' exposure. However, its performance during the shorter exposure periods was better than that of the copper clad 1100 aluminum. This difference can be attributed to the formation of an active intermetallic compound in the copper clad 1100 aluminum system.

Lead-coated copper-clad 5052 aluminum (Table A39) had better resistance to delamination and tunneling than the uncoated combination (Table A38b). The specimens in Fig. 10 after 15 years' exposure show that the most significant damage was due to complete corrosion of alumi-



FIG. 10—Appearance of lead coated Copper/5052 Aluminum/Copper after 15 years' exposure.

num at the edge rather than the tunneling that predominated with bare copper-clad aluminum. Apparently the lead coating is a less effective cathode for accelerating corrosion of the aluminum substrate than copper.

Summary and Conclusions

Based upon steel mass loss, the relative corrosivity of the test sites in this program was

Kure Beach (24 m) > Kure Beach (240 m) > Newark > Attleboro > Houston

> Miami (coastal) = Miami (inland) > Dallas > Anaheim

Stainless steels exhibited slight rust staining with Type 321 being the most resistant. Copper and brass alloys developed a protective patina, which resulted in a decreasing corrosion rate with increased exposure time. The formation of the green patina occurred more slowly in chloride-containing environments. Brasses tended to have lower corrosion rates in marine environments and higher corrosion rates in industrial environments.

Clad metals may be susceptible to galvanically induced localized corrosion such as galvanic pitting, tunneling, and delamination. These effects may influence mass change data such that it can be misleading. The rating system in Table 3 in conjunction with mass change data can describe the performance of clad metals. Clad metal systems (such as copper/321SS/copper) can be designed to resist galvanically induced localized corrosion.

The galvanic couple between nickel and steel is less severe than the couple between copper and steel. Increasing the thickness of the steel substrate reduced the severity of galvanic effects. The use of CORTEN as a substrate to replace steel does not have any beneficial effects. In marine environments, copper clad stainless steels may be susceptible to galvanically induced localized corrosion of the substrate. This does not occur with copper-clad type 321 stainless steel.

The galvanic couple between stainless steel and aluminum in a single clad configuration is a mild one. In general, tunneling and delamination do not occur in the single clad configuration but do occur in the double clad configuration. The metallurgy of the stainless steel to aluminum bond appears to be the key to delamination resistance. The formation of active intermetallic compounds degrades the performance of this system.

Copper clad aluminums are highly susceptible to galvanically induced localized corrosion. These systems should not be boldly exposed to corrosive atmospheres or weather. Improvement in performance can be obtained in the bonding process by avoiding the formation of intermetallics. The atmospheric corrosion resistance of substrates with copper claddings decreases in the order

stainless steel > steel > aluminum

(Appendix tables follow, pp. 160-189; References, p. 190)

APPENDIX

			Exposure Tim	e, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro	13.70	16.20	17.20	30.90	56.30
Dallas	2.40	5.90	9.70	14.48	12.60
Houston	6.80	23.20		26.70	
Anaheim	1.30	3.10	6.60	6.70	
Miami (inland)	4.00	6.30	10.00	18.90	25.10
Miami (coastal)	5.60	7.80	11.50	18.90	25.10
Newark	14.20	24.00	23.70	36.00	34.90
Kure Beach (80-ft)					
Kure Beach (800-ft)	9.80	24,70	>50		

TABLE Ala-Mass loss (grams) for 1006 steel.

TABLE A1b—Corrosion ratings for 1006 steel.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	31 XXXX	30 XXXX	42 XXXX	43 XXXX	55 XXXX		
Dallas	10 XXXX	20 XXXX	42 XXXX	43 XXXX	54 XXXX		
Houston	21 XXXX	32 XXXX		44 XXXX			
Anaheim	10 XXXX	22 XXXX	32 XXXX	33 XXXX			
Miami (inland)	21 XXXX	32 XXXX	40 XXXX	42 XXXX	54 XXXX		
Miami (coastal)	31 XXXX	32 XXXX	40 XXXX	42 XXXX	55 XXXX		
Newark	31 XXXX	43 XXXX	44 XXXX	44 XXXX	54 XXXX		
Kure Beach (80-ft)							
Kure Beach (800-ft)	21 XXXX	45 XXXX	55 XXXX				

NOTE: See Table 3 for explanation of rating system.

Site	Exposure Time, Years							
	0.5	1.5	3.5	7.5	15			
Attleboro								
Dallas	2.90	5.80	8.20					
Houston								
Anaheim	2.60	4.10	5.70					
Miami (inland)	3.50	5.80	8.50	• • •				
Miami (coastal)	3.70	4.80	7.00					
Newark	8.90	9.60	12.50		• • •			
Kure Beach (80-ft)	8.70	11.20	18.90					
Kure Beach (800-ft)	7.50	8.30	15.50					

TABLE A2a-Mass loss (grams) for Corten.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	10 XXXX	30 XXXX	32 XXXX				
Houston							
Anaheim	10 XXXX	20 XXXX	22 XXXX				
Miami (inland)	20 XXXX	30 XXXX	32 XXXX				
Miami (coastal)	20 XXXX	32 XXXX	32 XXXX				
Newark	20 XXXX	32 XXXX	32 XXXX				
Kure Beach (80-ft)	20 XXXX	30 XXXX	33 XXXX				
Kure Beach (800-ft)	20 XXXX	30 XXXX	32 XXXX				

TABLE A2b—Corrosion ratings for Corten.

TABLE A3a-Mass loss (grams) for type 409 stainless steel.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.15	0	0.10	0.10			
Dallas	0	0.20	0.10	0	0.10		
Houston	0	0.10	0.10	0			
Anaheim	0	0.10	0	0			
Miami (inland)	0	0	0.10	0	0		
Miami (coastal)	0	0	0.10	0	0.20		
Newark	0	0.10	0	0	0		
Kure Beach (80-ft)	0.20	0	0.20	0.20	0.40		
Kure Beach (800-ft)	0.20	0	0.10	0	0.10		

TABLE A3b—Corrosion ratings for type 409 stainless steel.

Site	Exposure Time, Years							
	0.5	1.5	3.5	7.5	15			
Attleboro	01 XXXX	01 XXXX	02 XXXX	02 XXXX				
Dallas	01 XXXX	02 XXXX	03 XXXX	02 XXXX	12 XXXX			
Houston	00 XXXX	02 XXXX	02 XXXX	02 XXXX				
Anaheim	01 XXXX	01 XXXX	01 XXXX	02 XXXX				
Miami (inland)	01 XXXX	01 XXXX	03 XXXX	13 XXXX	13 XXXX			
Miami (coastal)	00 XXXX	02 XXXX	04 XXXX	23 XXXX	32 XXXX			
Newark	00 XXXX	03 XXXX	03 XXXX	02 XXXX	12 XXXX			
Kure Beach (80-ft)	02 XXXX	02 XXXX	12 XXXX	23 XXXX	33 XXXX			
Kure Beach (800-ft)	01 XXXX	02 XXXX	12 XXXX	22 XXXX	32 XXXX			

Site Attleboro Dallas Houston Anaheim Miami (inland) Miami (coastal)	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0	0	0.01	0.10		
Dallas	0	0	0	+0.02	0		
Houston	0	0	0	0			
Anaheim	0	0	0	0			
Miami (inland)	0	0	0	0	0		
Miami (coastal)	0	0.10	0	0	0		
Newark	0	0	0	0.01	0		
Kure Beach (80-ft)	0	0	0	0	0		
Kure Beach (800-ft)	0	-	0	+0.05	0		

TABLE A4a-Mass loss (grams) for type 430 stainless steel.

TABLE A4b-Corrosion ratings for type 430 stainless steel.

Site	Exposure Time, Years							
	0.5	1.5	3.5	7.5	15			
Attleboro	01 XXXX	00 XXXX	02 XXXX	12 XXXX	22 XXXX			
Dallas	00 XXXX	01 XXXX	02 XXXX	12 XXXX	22 XXXX			
Houston	00 XXXX	01 XXXX	01 XXXX	12 XXXX				
Anaheim	00 XXXX	00 XXXX	01 XXXX	12 XXXX				
Miami (inland)	00 XXXX	01 XXXX	02 XXXX	12 XXXX	02 XXXX			
Miami (coastal)	00 XXXX	01 XXXX	12 XXXX	22 XXXX	22 XXXX			
Newark	00 XXXX	00 XXXX	00 XXXX	10 XXXX	12 XXXX			
Kure Beach (80-ft)	01 XXXX	02 XXXX	12 XXXX	22 XXXX	32 XXXX			
Kure Beach (800-ft)	00 XXXX		12 XXXX	22 XXXX	12 XXXX			

TABLE A5a-Mass loss (grams) for type 321 stainless steel.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.20	0.03	0	0	0		
Dallas	0	0	0	0	0		
Houston	0	0.20	0	0			
Anaheim	0	0	0	0	•••		
Miami (inland)	0	0.10	0	0	0		
Miami (coastal)	0	0.10	0	0	0		
Newark	0	0	0	0	0		
Kure Beach (80-ft)	0	0.10	0	0	0		
Kure Beach (800-ft)	0	0.10	0	0	0		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
 Attleboro	 00 XXXX	00 XXXX	01 XXXX	01 XXXX	22 XXXX		
Dallas	00 XXXX	00 XXXX	01 XXXX	01 XXXX	11 XXXX		
Houston	00 XXXX	00 XXXX	00 XXXX	00 XXXX			
Anaheim	00 XXXX	00 XXXX	01 XXXX	01 XXXX			
Miami (inland)	00 XXXX	01 XXXX	01 XXXX	01 XXXX	02 XXXX		
Miami (coastal)	00 XXXX	02 XXXX	02 XXXX	02 XXXX	12 XXXX		
Newark	00 XXXX	00 XXXX	00 XXXX	10 XXXX	20 XXXX		
Kure Beach (80-ft)	00 XXXX	01 XXXX	02 XXXX	12 XXXX	23 XXXX		
Kure Beach (800-ft)	00 XXXX	01 XXXX	02 XXXX	02 XXXX	12 XXXX		

TABLE A5b—Corrosion ratings for type 321 stainless steel.

TABLE A6a—Mass loss (grams) for oxygen free copper.

Site	Exposure Time, Years							
	0.5	1.5	3.5	7.5	15			
Attleboro	0.45	0.45	0.90	1.52	2.93			
Dallas	0.20	0.10	0.85	1.0	1.70			
Houston	0.20		0.85					
Anaheim		0.30	0.45	0.70				
Miami (inland)	0.20	0.20	0.60	0.72	1.24			
Miami (coastal)			1.65	2.40	3.50			
Newark		0.55	1.40	2.00	3.83			
Kure Beach (80-ft)	0.8	1.10	2.55	3.10	3.40			
Kure Beach (800-ft)	0.8	1.10	2.05	3.10	3.60			

TABLE A6b—Corrosion ratings for oxygen free copper.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	10 XXXX	20 XXXX	20 XXXX	20 XXXX g	33 XXXX g		
Dallas	10 XXXX	10 XXXX	20 XXXX	20 XXXX g	20 XXXX g		
Houston	10 XXXX		20 XXXX				
Anaheim		10 XXXX	20 XXXX	20 XXXX g			
Miami (inland)	10 XXXX	10 XXXX	20 XXXX	20 XXXX g	30 XXXX g+br		
Miami (coastal)			20 XXXX	20 XXXX br	30 XXXX g+br		
Newark		20 XXXX	20 XXXX	20 XXXX g	30 XXXX g		
Kure Beach (80-ft)	10 XXXX	20 XXXX	20 XXXX	21 XXXX br	32 XXXX g+br		
Kure Beach (800-ft)	10 XXXX	20 XXXX	20 XXXX	21 XXXX br	32 XXXX br		

Note: g = green, br = brown, bl = black.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.30	0.60	0.86	1.70	3.08		
Dallas	0.20	0.30	0.90	1.19	1.87		
Houston	0.20	0.70	1.10	1.68			
Anaheim	0.0	0.20	0.40	0.68			
Miami (inland)	0.10	0.30	0.50	0,91	1.32		
Miami (coastal)	0.40	0.60	0.90	1.42	1.76		
Newark	0,30	0.80	1.20		4.62		
Kure Beach (80-ft)	0.50	0.80	1.10	1.90	2.86		
Kure Beach (800-ft)	0.50	0.70	1.10	1.54	3.08		

TABLE A7a-Mass loss (grams) for commercial bronze (90 Cu 10 Zn).

TABLE A7b—Corrosion ratings for commercial bronze (90 Cu 10 Zn).

Site	Exposure Time, Years							
	0.5	1.5	3,5	7.5	15			
Attleboro	10 XXXX	20 XXXX	20 XXXX	20 XXXX g	32 XXXX g			
Dallas	10 XXXX	10 XXXX	20 XXXX	20 XXXX g	21 XXXX g			
Houston	10 XXXX	20 XXXX	30 XXXX	20 XXXX g				
Anaheim	10 XXXX	10 XXXX	10 XXXX	20 XXXX g				
Miami (inland)	10 XXXX	10 XXXX	20 XXXX	20 XXXX bi	30 XXXX bl			
Miami (coastal)	10 XXXX	20 XXXX	20 XXXX	20 XXXX br	31 XXXX br			
Newark	10 XXXX	20 XXXX	30 XXXX	20 XXXX g	32 XXXX g			
Kure Beach (80-ft)	10 XXXX	20 XXXX	30 XXXX	20 XXXX br	30 XXXX br			
Kure Beach (800-ft)	10 XXXX	20 XXXX	30 XXXX	20 XXXX br	31 XXXX br			

Note: g = green, br = brown, bl = black.

Site	Exposure Time, Years							
	0.5	1.5	3.5	7.5	15			
Attleboro								
Dallas	0.10	0.50	0.60	0.82	1,76			
Houston	0.20	0.80	1.10	2.01				
Anaheim	0.20	0.40	0.40	0.79				
Miami (inland)	0.10	0.40	0.50	0.76	1.57			
Miami (coastal)	0.40	0.80	0.70	1.34	1.76			
Newark	0.40	1.00	1.40	2,82	5,00			
Kure Beach (80-ft)	0.40	1.10	0.90	2.18	3.04			
Kure Beach (800-ft)	0.30	0.90	1.10	1.90				

TABLE A8a-Mass loss (grams) for 85-15 brass.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro				 , <i>.</i> ,			
Dallas	10 XXXX	10 XXXX	10 XXXX	20 XXXX g	21 XXXX g		
Houston	10 XXXX	20 XXXX	20 XXXX	20 XXXX g			
Anaheim	10 XXXX	20 XXXX	10 XXXX	20 XXXX g			
Miami (inland)	10 XXXX	10 XXXX [.]	10 XXXX	20 XXXX bi	31 XXXX g+br		
Miami (coastal)	10 XXXX	20 XXXX	20 XXXX	20 XXXX br	31 XXXX br		
Newark	10 XXXX	20 XXXX	20 XXXX	20 XXXX g	32 XXXX g		
Kure Beach (80-ft)	10 XXXX	20 XXXX	20 XXXX	20 XXXX br	30 XXXX br		
Kure Beach (800-ft)	10 XXXX	20 XXXX	20 XXXX	20 XXXX br	31 XXXX g+br		

TABLE A8b—Corrosion ratings for 85-15 brass.

Note: g = green, br = brown, bl = black.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	0.50	0.55	1.30	2.30	3.91		
Dallas	0.10	0.50	0.85	1.05	1.53		
Houston	0.20	0.80	1.30	1.97			
Anaheim	0.20	0.30	0.40	0.98			
Miami (inland)	0.30	0.10	0.50	0.58	1.28		
Miami (coastal)		0.30	0.65	0.75	1.36		
Newark	0.35	0.85	2.60	3.18	5.28		
Kure Beach (80-ft)	0.50	0.50	1.00	1.18	2.04		
Kure Beach (800-ft)	0.50	0.40	0.80	1.21	2.21		

TABLE A9a-Mass loss (grams) for 70-30 brass.

TABLE A9b—Corrosion ratings for 70-30 brass.

	Exposure Time, Years							
Site	0.5	1.5	3.5	7.5	15			
Attleboro	10 XXXX	20 XXXX	20 XXXX	20 XXXX g	32 XXXX g			
Dallas	10 XXXX	20 XXXX	20 XXXX	20 XXXX g+br	21 XXXX g+br			
Houston	10 XXXX	20 XXXX	20 XXXX	20 XXXX g				
Anaheim	10 XXXX	10 XXXX	10 XXXX	20 XXXX g+br				
Miami (inland)	10 XXXX	10 XXXX	10 XXXX	20 XXXX g+bl	20 XXXX br			
Miami (coastal)		10 XXXX	10 XXXX	20 XXXX br	30 XXXX br			
Newark	10 XXXX	20 XXXX	20 XXXX	20 XXXX g	30 XXXX g			
Kure Beach (80-ft)	10 XXXX	10 XXXX	10 XXXX	20 XXXX br	30 XXXX br			
Kure Beach (800-ft)	10 XXXX	10 XXXX	10 XXXX	20 XXXX br	31 XXXX br			

Note: g = green, br = brown, bl = black.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	0.40	0.50	0.80	1.42	2.78		
Dallas	• • •						
Houston	• • •						
Anaheim	0	0.10	0.10	0.23			
Miami (inland)	0	0	0.05	0.13	0.33		
Miami (coastal)	0	Ō	0.05	0.25	0.56		
Newark	0.40	0.60	1.30	1.80	2.55		
Kure Beach (80-ft)	0.20	0.10	0.25	0.52	1.66		
Kure Beach (800-ft)	0.10	0.10	0.25	0.39	1.22		

TABLE A10a—Mass loss (grams) for nickel.

TABLE A10b—Corrosion ratings for nickel.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7,5	15		
Attleboro	10 XXXX	11 XXXX	20 XXXX		31 XXXX		
Dallas							
Houston							
Anaheim	00 XXXX	10 XXXX	10 XXXX	20 XXXX			
Miami (inland)	00 XXXX	01 XXXX	12 XXXX	12 XXXX	10 XXXX		
Miami (coastal)	01 XXXX	11 XXXX	11 XXXX	11 XXXX	20 XXXX		
Newark	10 XXXX	10 XXXX	20 XXXX	20 XXXX	20 XXXX		
Kure Beach (80-ft)	11 XXXX	11 XXXX	12 XXXX	20 XXXX	20 XXXX		
Kure Beach (800-ft)	11 XXXX	11 XXXX	12 XXXX	20 XXXX	31 XXXX		

TABLE Alla-Mass loss (grams) for 1100 aluminum.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.10	+0.50	0.32	+0.60		
Dallas	0	0.10	+0.70	0.48	+0.10		
Houston	0	0.10	+0.10	0,06			
Anaheim	0	0.10	0	0.10			
Miami (inland)	0	0	0	0	+0.1		
Miami (coastal)	0	0.10	0	0.02	0		
Newark	0	0.10	0	0.16	0.10		
Kure Beach (80-ft)	0	0	+0.10	0.20	+0.20		
Kure Beach (800-ft)	Ō	0.10	0	0.16	+0.10		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	01 XXXX	02 XXXX	22 XXXX	22 XXXX	33 XXXX		
Dallas	01 XXXX	02 XXXX	12 XXXX	12 XXXX	22 XXXX		
Houston	02 XXXX	02 XXXX	02 XXXX	12 XXXX			
Anaheim	00 XXXX	01 XXXX	01 XXXX	12 XXXX	• • •		
Miami (inland)	02 XXXX	01 XXXX	02 XXXX	12 XXXX	22 XXXX		
Miami (coastal)	00 XXXX	02 XXXX	12 XXXX	12 XXXX	22 XXXX		
Newark	02 XXXX	01 XXXX	02 XXXX	12 XXXX	32 XXXX		
Kure Beach (80-ft)	02 XXXX	03 XXXX	13 XXXX	13 XXXX	33 XXXX		
Kure Beach (800-ft)	02 XXXX	02 XXXX	02 XXXX	12 XXXX	22 XXXX		

TABLE A11b—Corrosion ratings for 1100 aluminum.

TABLE A12a-Mass loss (grams) for 3003 aluminum.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0	0.01	0	+0.63	0.88		
Dallas	0	0.1	0	+0.09	0.40		
Houston	0	0.1	0	0.22			
Anaheim	0	0.1	0	0.04			
Miami (inland)	0	0.1	0.1	0.04	0.12		
Miami (coastal)	0	0.0	0	0.09	0.16		
Newark	0	0.1	0	0.02	0.40		
Kure Beach (80-ft)	0	0.0	0.15	+0.18	0.40		
Kure Beach (800-ft)	0	0.1	0	+0.13	0.40		

TABLE A12b—Corrosion ratings for 3003 aluminum.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	02 XXXX	01 XXXX	02 XXXX	22 XXXX	33 XXXX		
Dallas	01 XXXX	02 XXXX	02 XXXX	22 XXXX	22 XXXX		
Houston	02 XXXX	02 XXXX	12 XXXX	12 XXXX			
Anaheim	01 XXXX	01 XXXX	02 XXXX	12 XXXX			
Miami (inland)	00 XXXX	01 XXXX	12 XXXX	12 XXXX	32 XXXX		
Miami (coastal)	01 XXXX	02 XXXX	02 XXXX	12 XXXX	32 XXXX		
Newark	00 XXXX	02 XXXX	11 XXXX	22 XXXX	32 XXXX		
Kure Beach (80-ft)	12 XXXX	02 XXXX	12 XXXX	22 XXXX	31 XXXX		
Kure Beach (800-ft)	02 XXXX	02 XXXX	12 XXXX	12 XXXX	32 XXXX		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.1	0.05	+0.10	0.35	0.91		
Dallas	0	0	+0.40	+0.05	0.48		
Houston	0	0.10	0	+0.24			
Anaheim	0	0.10	+0.10	0.10			
Miami (inland)	0	0	0	0.02	0.10		
Miami (coastal)	0	0	0	0.11	0.20		
Newark	Ō	0	+0.15	0.19	0.40		
Kure Beach (80-ft)	0	0	+0.10	0.19	0.30		
Kure Beach (800-ft)	Ő	0.10	0	0.15	0.40		

TABLE A13a-Mass loss (grams) for 5052 aluminum.

TABLE A13b—Corrosion ratings for 5052 aluminum.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	02 XXXX	02 XXXX	02 XXXX	22 XXXX	33 XXXX		
Dallas	02 XXXX	02 XXXX	02 XXXX	12 XXXX	22 XXXX		
Houston	02 XXXX	02 XXXX	02 XXXX	12 XXXX	• • • •		
Anaheim	02 XXXX	02 XXXX	02 XXXX	12 XXXX	• • •		
Miami (inland)	01 XXXX	02 XXXX	02 XXXX	12 XXXX	32 XXXX		
Miami (coastal)	02 XXXX	02 XXXX	02 XXXX	12 XXXX	32 XXXX		
Newark	01 XXXX	12 XXXX	02 XXXX	22 XXXX	32 XXXX		
Kure Beach (80-ft)	12 XXXX	12 XXXX	02 XXXX	22 XXXX	31 XXXX		
Kure Beach (800-ft)	02 XXXX	12 XXXX	02 XXXX	12 XXXX	32 XXXX		

TABLE A14a-Mass loss (grams) for copper/1006 steel/copper.

Exposure Time, Years						
0.5	1.5	3.5	7.5	15		
0.50	0.75	1.20	2.02	destroyed		
0.20	0.60	0.80	1.10	1.91		
0.30	0.70	1.05	1.88			
0.10	0.30	0.40	0.62	• • •		
0.10	0.40	0.60	1.44	3.33		
0.55	0.85	0.55	2.08	2.89		
0.30	1.05	1.70	1.19	5.98		
0.60	1.10	0.90	5.10	destroyed		
0.50	1.10	1.20	3.10	6.47		
	0.5 0.20 0.30 0.10 0.55 0.30 0.60 0.50	0.5 1.5 0.50 0.75 0.20 0.60 0.30 0.70 0.10 0.30 0.55 0.85 0.30 1.05 0.60 1.10 0.50 1.10	Exposure Tim 0.5 1.5 3.5 0.50 0.75 1.20 0.20 0.60 0.80 0.30 0.70 1.05 0.10 0.30 0.40 0.10 0.40 0.60 0.55 0.85 0.55 0.30 1.05 1.70 0.60 1.10 0.90 0.50 1.10 1.20	Exposure Time, Years 0.5 1.5 3.5 7.5 0.50 0.75 1.20 2.02 0.20 0.60 0.80 1.10 0.30 0.70 1.05 1.88 0.10 0.30 0.40 0.62 0.10 0.40 0.60 1.44 0.55 0.85 0.55 2.08 0.30 1.05 1.70 1.19 0.60 1.10 0.90 5.10 0.50 1.10 1.20 3.10		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 200	200 201	200 301	202 301	destroyed		
Dallas	100 100	200 201	201 201	201 301	231 522		
Houston	100 100	200 201	201 201	201 201			
Anaheim	100 100	100 100	200 201	201 201			
Miami (inland)	100 100	201 201	220 301	201 301	344 422		
Miami (coastal)	100 100	200 201	201 301	201 301	313 422		
Newark	100 100	200 201	200 301	201 301	443 444		
Kure Beach (80-ft)	100 200	201 222	201 302	201 302	destroyed		
Kure Beach (800-ft)	100 100	200 201	200 302	201 302	314 543		

TABLE A14b—Corrosion ratings for copper/1006 steel/copper.

TABLE A15a-Mass loss (grams) for bronze/1006 steel/bronze.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	0.25	0.40	1.05	1.45			
Houston	0.30	0.50	1.20	· · ·			
Anaheim	0.15	0.20	0.50	0.71			
Miami (inland)							
Miami (coastal)							
Newark							
Kure Beach (80-ft)							
Kure Beach (800-ft)				•••			

TABLE A15b—Corrosion ratings for bronze/1006 steel/bronze.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	100 100	100 100	200 301	200 311			
Houston	100 100	100 100	200 300				
Anaheim	100 100	100 100	200 200	200 200			
Miami (inland)							
Miami (coastal)							
Newark							
Kure Beach (80-ft)							
Kure Beach (800-ft)				• • •			

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	0.50	1.50	2.30	2.48	4.88		
Dallas	1.10	0.50	0.70	1.10	2.18		
Houston	0.30	0.90	1.10	1.15			
Anaheim	0.10	0.30	0.40				
Miami (inland)	0	0.40	+0.50	0.86	1.85		
Miami (coastal)	0.30	0.60	0.70	0.89	1.98		
Newark	0.30	0.35	1.60	2.89	5.21		
Kure Beach (80-ft)	0.40	0.80	+0.30	2.10	3.17		
Kure Beach (800-ft)	0.30	0.90	0.70	1.97	1.06		

TABLE A16a-Mass loss (grams) for 85-15 brass/1006 steel/85-15 brass.

TABLE A16b-Corrosion ratings for 85-15 brass/1006 steel/85-15 brass.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 100	200 100	200 211	200 211	323 512		
Dallas	100 100	100 100	200 211	201 211	211 422		
Houston	100 100	200 201	200 311	200 211			
Anaheim	100 100	100 100	200 211	•••			
Miami (inland)	100 100	100 100	200 211	200 211	301 422		
Miami (coastal)	100 100	100 200	200 200	200 200	211 200		
Newark	100 100	100 100	200 211	200 311	301 312		
Kure Beach (80-ft)	100 100	200 200	200 311	200 210	311 210		
Kure Beach (800-ft)	100 100	200 200	200 211	200 311	201 522		

TABLE A17a—Mass loss (grams) for nickel/1006 steel/nickel.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.50	0.90	1.20	1.93	3.74		
Dallas	• • • •	0.20	0.70	1.01	1.53		
Houston	0.0	0.50	0.40	•••	• • •		
Anaheim	0.20	0.20	0.20	0.29			
Miami (inland)	0	0.20	0	0.25	0.51		
Miami (coastal)	• • • •	0.20	0.20	0.37	0.35		
Newark	0.50	1.30	1.90	3.23	3.23		
Kure Beach (80-ft)	0.20	0.70	0.70	1.43	2.72		
Kure Beach (800-ft)	0	0.40	0.50	1.11	3.06		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 100	200 200	200 200	200 200	311 411		
Dallas		100 100	200 200	200 200	200 200		
Houston	000 100	100 100	100 200				
Anaheim	010 100	100 100	100 200	200 200			
Miami (inland)	000 100	120 200	000 200	100 200	200 410		
Miami (coastal)		120 200	010 200	100 200	200 300		
Newark	100 100	200 200	201 200	200 200	300 310		
Kure Beach (80-ft)	000 100	220 200	100 200	200 200	311 411		
Kure Beach (800-ft)	000 100	120 200	100 200	200 200	312 420		

TABLE A17b—Corrosion ratings for nickel/1006 steel/nickel.

TABLE A18a—Mass loss (grams) for copper/corten/copper (0.015).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro				•••			
Dallas	0.20	0.35	0.70	0.97	1.71		
Houston	0.30	0.30	1.05	• • •			
Anaheim	0.15	0.25	0.45				
Miami (inland)	0.20	0.20	0.80	2.22			
Miami (coastal)	0.40	0.60	1.10				
Newark	0.40	0.60	0.90	2.23			
Kure Beach (80-ft)	0.60	1.75	+7.40	+3.90			
Kure Beach (800-ft)	0.50	0.70	1.60				

TABLE A18b—Corrosion ratings for copper/corten/copper (0.015).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro			<u>_</u>				
Dallas	100 100	200 210	201 321	201 322			
Houston	100 210	201 320	201 322	201 333			
Anaheim	100 100	100 200	201 211				
Miami (inland)	100 100	100 200	102 333	201 555			
Miami (coastal)	100 100	200 210	101 322	201 444			
Newark	100 100	200 200	201 311	203 322			
Kure Beach (80-ft)	101 222	201 433	201 444	204 555			
Kure Beach (800-ft)	101 210	201 332	201 433	202 444			
	Exposure Time, Years						
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Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	0.25	0.30	0.95	1.25	2.78		
Houston	0.30	0.30	0.80				
Anaheim	0.30	0.15	0.50				
Miami (inland)	0.35	0.90	0.45		1.54		
Miami (coastal)	0.35	+0.10	1.10	1.67	2.02		
Newark	0.45	0.50	1.35	2.17	3.46		
Kure Beach (80-ft)	0.70	0.80	2.10				
Kure Beach (800-ft)	0.70	0.65	1.35	2.16	4.22		

TABLE A19a-Mass loss (grams) for copper/corten/copper (0.030).

TABLE A19b—Corrosion ratings for copper/corten/copper (0.030).

Site Attleboro Dallas Houston	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	100 100	100 200	200 210	200 210	211 321		
Houston	100 100	100 200	200 210				
Anaheim	100 100	100 200	200 200				
Miami (inland)	100 100	200 200	201 310	201 310	202 322		
Miami (coastal)	100 100	100 200	101 330	201 210	311 544		
Newark	100 100	100 200	200 200	200 200	301 311		
Kure Beach (80-ft)	100 100	200 211	201 311	201 333			
Kure Beach (800-ft)	100 100	200 200	201 311	201 444	214 333		

TABLE A20a-Mass loss (grams) for 85-15 brass/corten/85-15 brass.

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	0.15	0.20	0.45	0.93	0.92		
Houston	0.30	0.50	1.10	0.95			
Anaheim	0.20	0.20	0.45	0.52			
Miami (inland)	0.20	0.15	0.30		0.92		
Miami (coastal)	0.25	0.10	0.10	+0.15	+0.10		
Newark	0.40	0.60	1.60	3.10	3.73		
Kure Beach (80-ft)	0.40	0.40	+1.10	+6.19			
Kure Beach (800-ft)	0.35	0.40	0.45	+1.10	+2.53		

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro		-					
Dallas	100 100	200 121	200 221	200 231	211 241		
Houston	100 100	200 121	200 221	200 201			
Anaheim	100 100	200 100	200 100	200 230			
Miami (inland)	100 110	200 220	200 230		200 131		
Miami (coastal)	100 210	200 232	201 333	201 444	301 344		
Newark	100 000	200 000	200 100	200 100	320 100		
Kure Beach (80-ft)	100 210	200 332	201 333	201 444			
Kure Beach (800-ft)	100 210	200 331	201 331	201 444	433 344		

TABLE A20b-Corrosion ratings for 85-15 brass/corten/85-15 brass.

TABLE A21a-Mass loss (grams) for bronze/corten/bronze.

	Exposure Time, Years						
Site	0.5	1.5	3.5	ne, Years 7.5 1.10 7.82 3.29 0.85 2.71 6.12	15		
Attleboro		- 					
Dallas	0.20	0.30	1.10	1.10	1.22		
Houston	0.30	0.45	1.35	7.82			
Anaheim	0.15	0.20	0.40				
Miami (inland)	0.20	0.35	0,90	3.29			
Miami (coastal)	0.30	0.40	0.70	0.85	3.15		
Newark	0.40	0.70	1.50	2.71	3.40		
Kure Beach (80-ft)	0.60	0.65	+3.60	6.12	destroyed		
Kure Beach (800-ft)	0.40						

TABLE A21b—Corrosion ratings for bronze/corten/bronze.

	Exposure Time, Years							
Site	0.5	1.5	3.5	7.5	15			
Attleboro								
Dallas	100 100	200 210	200 322	201 333	211 444			
Houston	100 110	201 311	201 322	201 333	· · · ·			
Anaheim	100 100	201 311	200 211					
Miami (inland)	100 100	201 311	201 422	201 444				
Miami (coastal)	100 110	200 210	201 322	201 333	301 454			
Newark	100 100	200 301	201 322	204 322	444 433			
Kure Beach (80-ft)	100 211	201 322	202 433	202 555	555 544			
Kure Beach (800-ft)	100 210							

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	• • •	0.40	0.90	1.20	2.16		
Houston		0.40	0.90		•••		
Anaheim	0.20	0.25	0.40		•••		
Miami (inland)	0.10	0.30	0.55	0.83	1.24		
Miami (coastal)	0.30	0.55	1.20	1.26	0.71		
Newark	0.30	0.55	1.40				
Kure Beach (80-ft)	0.70		1.30				
Kure Beach (800-ft)	0.55	0.80	1.35	1.30	1.17		

TABLE A22a-Mass loss (grams) for copper/409 stainless steel/copper (0.015).

TABLE A22b—Corrosion ratings for copper/409 stainless steel/copper (0.015).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas		200 110	200 210	200 210	211 220		
Houston		200 110	200 110	• • •			
Anaheim	100 000	100 000	200 000				
Miami (inland)	100 000	100 110	101 220	200 200	300 121		
Miami (coastal)	100 100	200 210	201 330	201 330	311 441		
Newark	100 000	200 320	200 000	200 000			
Kure Beach (80-ft)	100 100		203 330	204 340			
Kure Beach (800-ft)	100 100	200 210	202 220	202 330	343 211		

TABLE A23a—Mass loss (grams) for copper/409 stainless steel/copper (0.030).

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	•••	0.40	0.80	0.97	0.47		
Houston		0.30	0.80		• • •		
Anaheim	0.25	0.25	0.45	0.70	• • •		
Miami (inland)	0.20	0.25	0.45	0.66	1.21		
Miami (coastal)	0.40	0.50	1.75	1.77	0.56		
Newark	0.40	0.45	1.30	2.38	2.60		
Kure Beach (80-ft)	0.75	0.90	1.50	1.93	0.19		
Kure Beach (800-ft)	0.65	0.82	1.20	1.02	+0.28		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas		100 000	200 210	200 220	211 220		
Houston		101 100	200 220				
Anaheim	100 000	100 000	200 000	200 000			
Miami (inland)	100 000	100 120	201 220	201 230	201 121		
Miami (coastal)	100 100	100 120	201 220	201 230	211 341		
Newark	100 000	100 000	200 000	200 000	310 100		
Kure Beach (80-ft)	100 100	101 220	201 320	201 330	312 332		
Kure Beach (800-ft)	100 100	100 210	201 320	201 330	212 220		

TABLE A23b—Corrosion ratings for copper/409 stainless steel/copper (0.030).

TABLE A24a—Mass loss (grams) for copper/409 stainless steel/copper (scribed).

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas							
Houston							
Anaheim		0.20	0.50	0.63			
Miami (inland)		0.20	0.50	0.53	0.74		
Miami (coastal)		0.20	0.00	0.00			
Newark	0.40	0.60	1 40		4 19		
Kure Beach (80-ft)	5.70	1.00	1.50	1.63	0.09		
Kure Beach (800-ft)		0.65	1.10	1.02	+0.65		

TABLE A24b-Corrosion ratings for copper/409 stainless steel/copper (scribed).

	Exposure Time, Years							
Site	0.5	1.5	3.5	7.5	15			
Attleboro								
Dallas								
Houston								
Anaheim		100 000	200 000	200 000				
Miami (inland)		100 110	201 220	201 230	201 121			
Miami (coastal)								
Newark	100 000	200 000	300 000	300 000	310 100			
Kure Beach (80-ft)		200 320	201 330	203 330	313 332			
Kure Beach (800-ft)		200 320	201 320	202 330	313 221			

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	0.10	0.30	0.50	0.65	1.18		
Houston	0.25	1.20	0.95				
Anaheim	0.20	0.30	0.40				
Miami (inland)	0.20	0.20	0.80	0.48	0.90		
Miami (coastal)	0.35	0.30	0.20	0.20	+0.14		
Newark	0.35	0.65	1.25	2.63	3.52		
Kure Beach (80-ft)	0,50	0.50	0.40	+3.04	+8.98		
Kure Beach (800-ft)	0.40	0.50	0.40	0.18	+2.12		

TABLE A25a—Mass loss (grams) for 85-15 brass/409 stainless steel/85-15 brass.

TABLE A25b—Corrosion ratings for 85-15 brass/409 stainless steel/85-15 brass.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	100 000	200 121	200 231	201 241	211 241		
Houston	100 000	200 121	200 120				
Anaheim	100 000	200 000	200 000				
Miami (inland)	100 110	200 221	201 220	201 230	301 141		
Miami (coastal)	100 110	200 231	201 231	201 241	301 244		
Newark	100 000	200 000	200 000	200 000	321 100		
Kure Beach (80-ft)	101 210	201 321	201 331	201 441	543 344		
Kure Beach (800-ft)	101 210	201 321	201 331	201 441	323 133		

TABLE A26a—Mass loss (grams) for bronze/409 stainless steel/bronze.

Site Attleboro Dallas Houston Anahaim	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	• • •						
Dallas	0.20	0.30	0.45	0.63	1.03		
Houston	0.25	0.45	0.55	1.34			
Anaheim	0.20	0.20	0.40				
Miami (inland)	0.25	0.20	0.50	0.45	1.13		
Miami (coastal)	0.30	0.25	0.20	0.02	+0.14		
Newark	0.35	0.65	1.50	2.67	3.67		
Kure Beach (80-ft)	0.50	0.65	0.40	+3.48	+10.99		
Kure Beach (800-ft)	0.40	0.50	0.50	0.08	+1.88		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas	100 000	200 221	201 230	201 230	211 230		
Houston	100 000	200 121	200 120	200 220			
Anaheim	100 000	100 000	200 000				
Miami (inland)	100 110	100 220	101 320	201 330	301 341		
Miami (coastal)	100 110	200 332	201 322	201 442	301 244		
Newark	100 000	200 000	200 000	200 000	320 100		
Kure Beach (80-ft)	101 210	200 321	201 333	202 444	433 444		
Kure Beach (800-ft)	100 110	200 321	201 331	201 333	323 233		

TABLE A26b—Corrosion ratings for bronze/409 stainless steel/bronze.

TABLE A27a-Mass loss (grams) for coppper/430 stainless steel/copper.

Site Attleboro Dallas	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.40	0.40	0.80	1.43	2.70		
Dallas	0.10	0.30	0,0	0.71	1.20		
Houston	0.20	0.70	0.90	1.25			
Anaheim	0.10	0.40	0.40	0.69			
Miami (inland)	0.10	0.50	0.30	0.60	0.10		
Miami (coastal)	0.30	0.60	0.50	0.44	0.30		
Newark	0.20	0.70	1.30	2.37	3.90		
Kure Beach (80-ft)	0.50	0.90	0.90	0.57	+1.80		
Kure Beach (800-ft)	0.50	1.00	1.20	1.40	0.10		

TABLE A27b—Corrosion ratings for copper/430 stainless steel/copper.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 000	200 000	200 100	200 100	321 200		
Dallas	100 000	200 000	200 220	200 230	311 210		
Houston	100 100	200 110	200 000	200 000			
Anaheim	100 000	200 000	200 000	200 000			
Miami (inland)	100 100	200 120	200 230	200 220	200 221		
Miami (coastal)	100 210	201 230	202 341	200 343	302 344		
Newark	100 000	200 000	200 000	200 000	311 100		
Kure Beach (80-ft)	100 100	201 220	201 331	201 330	312 331		
Kure Beach (800-ft)	100 100	201 220	201 230	200 230	211 242		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro		0.85	1.50	2.11	3.28		
Dallas	0.20	0.40	1.00	1.33	1.64		
Houston	0.20	0.60	1.00	1.41			
Anaheim	0.20	0.30	0.45	0.69			
Miami (inland)	0.20	0.35	0.45	0.81	1.05		
Miami (coastal)	0.55	0.80	1.10	1.99	3.50		
Newark	0.35	0.80	1,45	2.42	3.54		
Kure Beach (80-ft)	0.45	1.00	1.60	2.70	3.39		
Kure Beach (800-ft)	0.45	0.90	1.35	2.02	3.62		

TABLE A28a-Mass loss (grams) for copper/321 stainless steel/copper.

TABLE A28b—Corrosion ratings for copper/321 stainless steel/copper.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 000	100 000	200 000	200 000	300 000		
Dallas	100 000	100 000	200 000	200 000	200 000		
Houston	100 000	100 000	200 000	200 000			
Anaheim	100 000	100 000	100 000	200 000			
Miami (inland)	100 000	100 000	100 000	200 000	200 000		
Miami (coastal)	100 000	100 000	200 000	200 000	300 000		
Newark	100 000	100 000	200 000	200 000	300 000		
Kure Beach (80-ft)	100 000	100 000	200 000	200 000	300 000		
Kure Beach (800-ft)	100 000	100 000	200 000	200 000	300 000		

TABLE A29a-Mass loss (grams) for 434 stainless steel/3003 aluminum (aluminum skyward).

	Exposure Time, Years							
Site Attleboro Dallas Houston Anaheim Miami (inland)	0.5	1.5	3.5	7.5	15			
Attieboro		0.2		0.34	+0.30			
Dallas	0	0.1	+0.4	0.16	+0.60			
Houston	0	0.1	0					
Anaheim	0	0.1	0	0.09				
Miami (inland)	0	0.1	0	0.02	0			
Miami (coastal)	0	0.1	0	0.01				
Newark	0	0.1	0	0.11	0.30			
Kure Beach (80-ft)	0	0		0.20	2.20			
Kure Beach (800-ft)	0	0.1	0	0.11	+1.68			

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	 	020 200		220 200	321 200		
Dallas	010 100	010 200	120 200	120 200	221 200		
Houston	010 100	010 100	020 200	120 200			
Anaheim	000 100	010 100	020 100	120 200			
Miami (inland)	010 100	010 200	110 100	120 200	220 200		
Miami (coastal)	010 100	010 200	110 100	120 200			
Newark	010 100	020 200	120 200	210 200	310 200		
Kure Beach (80-ft)	010 100	020 300		220 200	320 200		
Kure Beach (800-ft)	010 100	010 200	120 200	120 200	221 200		

TABLE A29b—Corrosion ratings for 434 stainless steel/3003 aluminum (aluminum skyward).

TABLE A29c-Mass loss (grams) for 434 stainless steel/3003 aluminum (stainless steel skyward).

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro	0	0.10		0.30	+0.50		
Dallas	0	0.10	+0.10	0.27	0		
Houston	0	0.10	0	0.23			
Anaheim	0	0.10	0	0.05	• • •		
Miami (inland)	0	0.10	0	0.01	0		
Miami (coastal)	0	0.10	0	0.08			
Newark	0	0	0	0.11			
Kure Beach (80-ft)	0	0	+0.15	0.28	+0.60		
Kure Beach (800-ft)	0	0	0	+0.11	1.12		

TABLE A29d—Corrosion ratings for 434 stainless steel/3003 aluminum (stainless steel skyward).

Site					
	0.5	1.5	3.5	7.5	15
Attleboro	000 000	000 000	022 000	010 000	111 200
Dallas	000 000	000 000	010 000	020 000	111 200
Houston	000 000	000 000	010 000		
Anaheim	000 000	000 000	010 000	010 000	
Miami (inland)	010 000	000 000	020 000	020 000	020 200
Miami (coastal)	010 000	000 000	020 000	020 000	
Newark	000 000	000 000	000 000	000 000	
Kure Beach (80-ft)	010 000	000 000	020 000	020 000	120 200
Kure Beach (800-ft)	000 000	000 000	020 000	020 044	120 355

	Exposure Time, Years						
Site	0.5	1.5	3.5	7.5	15		
Attleboro		0.02	0	0.20	0		
Dallas	0	0	+0.10	0.19	0.10		
Houston	0.10	+0.05	+0.10				
Anaheim		0	0				
Miami (inland)	0	0	0	+0.01			
Miami (coastal)	0	0	0	0.02	0		
Newark	0	0					
Kure Beach (80-ft)	0	0.10	+0.15	0	0		
Kure Beach (800-ft)	0	0	0	+0.06	0		

TABLE A30a—Mass loss (grams) for 434 stainless steel/5052 aluminum (aluminum skyward).

TABLE A30b—Corrosion ratings for 434 stainless steel/5052 aluminum (aluminum skyward).

Site	Exposute Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro		020 100	020 200	220 200	221 311		
Dallas	010 000	010 000	020 220	120 200	221 200		
Houston	020 100	020 200	020 110				
Anaheim		000 200	120 100				
Miami (inland)	000 100	010 100	020 000	120 100	321 200		
Miami (coastal)	020 100	020 200	020 100	120 200	221 200		
Newark							
Kure Beach (80-ft)	010 100	030 200	120 322	120 344	321 323		
Kure Beach (800-ft)	010 100	010 100	020 200	120 200	331 322		

TABLE A30c—Mass loss (grams) for 434 stainless steel/5052 aluminum (stainless steel skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.03	0	0.15			
Dallas	0.10	0.10	+0.30	0.10	0.10		
Houston	0.10	+0.05	0				
Anaheim	0	0.10	0				
Miami (inland)	0	0	0	0.01			
Miami (coastal)	0	0.10	0	0.06	0		
Newark	0	0					
Kure Beach (80-ft)	0	0.30	+0.25	+0.35	+0.40		
Kure Beach (800-ft)	0	0.10	0	0.10	0		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	010 000	000 000	021 000				
Dallas	000 000	000 000	021 000	020 200	121 200		
Houston	010 000	010 000	010 000				
Anaheim	010 000	010 000	010 000				
Miami (inland)	010 000	020 000	010 000	020 200			
Miami (coastal)	020 000	020 000	020 000	020 200	021 200		
Newark	000 000	000 000					
Kure Beach (80-ft)	020 000	010 000	021 000	120 344	121 323		
Kure Beach (800-ft)	010 000	010 000	010 000	121 200	121 311		

TABLE A30d—Corrosion ratings for 434 stainless steel/5052 aluminum (stainless steel skyward).

TABLE A31a-Mass loss (grams) for 304 stainless steel/3003 aluminum (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.10	0		0		
Dallas	0	0.10	+0.10	+0.10	0		
Houston	0	0.10	0	0.61			
Anaheim	0	0.10	0	0.05			
Miami (inland)	0	0.10	0	0	0.10		
Miami (coastal)	0	0.10	0	0.05	0		
Newark	0	0	0	0.04	0.40		
Kure Beach (80-ft)	0	0	+0.10	+0.09	0		
Kure Beach (800-ft)	0	0.10	+0.10	+0.12	0		

TABLE A31b-Corrosion ratings for 304 stainless steel/3003 aluminum (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	010 100	010 200	220 200		331 300		
Dallas	010 100	020 200	120 200	220 200	220 200		
Houston	010 100	010 200	120 100				
Anaheim	000 100	010 100	120 100	120 100			
Miami (inland)	010 100	020 200	120 100	120 200	221 100		
Miami (coastal)	010 200	021 200	020 300	120 200	321 200		
Newark	010 100	010 100	120 200	100 100	310 200		
Kure Beach (80-ft)	010 200	020 300	020 200	120 200	321 200		
Kure Beach (800-ft)	020 200	021 200	020 200	020 200	221 300		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.5	0	+0.05			
Dallas	0	0.10	+0.30	+0.09	0		
Houston	0	0	0				
Anaheim	0	0.10	0	+0.02			
Miami (inland)	0	0	0	+0.01	0		
Miami (coastal)	0	0	0	0.01	0		
Newark	0	0	0	0.02	0.30		
Kure Beach (80-ft)	0	0	+0.10	0.02	0.30		
Kure Beach (800-ft)	0	0	+0.10	+0.13	0		

TABLE A31c-Mass loss (grams) for 304 stainless steel/3003 aluminum (stainless steel skyward).

TABLE A31d-Corrosion ratings for 304 stainless steel/3003 aluminum (stainless steel skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	000 000	010 000	020 000	010 100			
Dallas	010 000	020 000	020 000	010 100	110 100		
Houston	000 000	010 000	010 000				
Anaheim	000 000	000 000	010 000	110 000			
Miami (inland)	000 000	010 000	010 000	110 100	111 100		
Miami (coastal)	000 000	021 000	020 000	110 100	111 100		
Newark	000 000	010 000	000 000	100 100	210 200		
Kure Beach (80-ft)	010 000	020 000	020 000	110 200	221 200		
Kure Beach (800-ft)	010 000	021 000	020 000	110 100	121 200		

TABLE A32a-Mass loss (grams) for 201 stainless steel/3003 aluminum (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0	0		0.30		
Dallas	0.10	0	+0.40	0.20	0.50		
Houston	0.10	+0.02	0				
Anaheim	0	0.10	0				
Miami (inland)	0	0.10	0.10	0.07	0		
Miami (coastal)	0	0.10	0	0.04	0.10		
Newark	0.10	0	0	0.06	0.21		
Kure Beach (80-ft)	0	0.10	0	0.21	0.30		
Kure Beach (800-ft)	0	0.10	0	0.11	0.30		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	020 100	020 100	020 200		322 200		
Dallas	010 100	000 000	020 200	200 200	311 200		
Houston	020 200	020 100	010 100				
Anaheim	000 100	020 100	010 100				
Miami (inland)	010 100	020 100	010 100	120 200	331 200		
Miami (coastal)	020 200	020 100	020 200	120 200	320 200		
Newark	010 100	020 100	020 200	200 200	310 200		
Kure Beach (80-ft)	010 100	020 200	020 300	120 200	321 200		
Kure Beach (800-ft)	020 100	020 100	020 200	120 200	221 200		

TABLE A32b—Corrosion ratings for 201 stainless steel/3003 aluminum (aluminum skyward).

TABLE A32c-Mass loss (grams) for 201 stainless steel/3003 stainless steel (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.10	0	0.12	0.40		
Dallas	0.10	0	+0.20	0.05	0.30		
Houston	0.10	+0.10	0				
Anaheim	0	0.10	0				
Miami (inland)	0	0.10	0.10	0.08	0.11		
Miami (coastal)	0	0.10	+0.10	0.09	0.22		
Newark	0.10	0	0	0.10	0.22		
Kure Beach (80-ft)	0	0.10	0	0.16	0.50		
Kure Beach (800-ft)	0	0.10	0	0.09	0.22		

TABLE A32d-Corrosion ratings for 201 stainless steel/3003 aluminum (stainless steel skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	000 000	000 000	010 000	020 222	121 200		
Dallas	000 000	000 000	020 000	020 200	121 200		
Houston	000 000	000 000	010 000				
Anaheim	000 000	000 000	010 000				
Miami (inland)	010 000	010 000	020 000	020 200	021 200		
Miami (coastal)	020 000	010 000	020 000	020 200	021 200		
Newark	000 000	000 000	000 000	100 100	211 200		
Kure Beach (80-ft)	010 000	000 000	020 000	020 200	121 200		
Kure Beach (800-ft)	010 000	000 000	010 000	020 200	021 200		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0	0	+0.30	+1.77	+0.2		
Dallas	0	0.1	0	+0.06	0		
Houston	0	0	0		••.		
Anaheim	0	0.15	0	+0.09			
Miami (inland)	0	0	+0.15	+0.62	+0.10		
Miami (coastal)	0	+0.10	+0.30	+0.52	+0.10		
Newark	0	0	+0.15	+0.90	+4.11		
Kure Beach (80-ft)	0	0	+0.10	2.12	0		
Kure Beach (800-ft)	0	0	+0.10	+0.75	+0.55		

TABLE A33a—Mass loss (grams) for 304 stainless steel/7072 aluminum/3004 aluminum/7072 aluminum/
304 stainless steel,

TABLE A33b—Corrosion ratings for 304 stainless steel/7072 aluminum/3004 aluminum/7072 aluminum/ 304 stainless steel.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	000 100	000 100	000 222	010 254	110 315		
Dallas	000 100	000 100	010 211	010 200	010 200		
Houston	010 100	000 100	010 200		• • •		
Anaheim	000 100	000 110	010 200	010 200	•••		
Miami (inland)	010 100	010 100	020 200	120 240	120 310		
Miami (coastal)	010 100	010 100	020 211	120 200	120 311		
Newark	000 100	010 110	000 211	100 555	112 000		
Kure Beach (80-ft)	010 100	010 110	020 233	120 255	221 355		
Kure Beach (800-ft)	000 100	010 233	020 233	020 244	021 355		

TABLE A34a-Mass loss (grams) for copper/1100 aluminum (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.20	0.20	0.20	0.34	1.75		
Dallas	• • •	0.30	+0.60	0.40	3.65		
Houston	0	0.30	0.20	0.66	• • •		
Anaheim	0.30	0.20	+0.20	0.66	• • •		
Miami (inland)	0	0.20	0	0.10	0.96		
Miami (coastal)	• • •	0.20	+0.10	0.81	2.62		
Newark	0.10	0.25	0.30	0,60	1.09		
Kure Beach (80-ft)	0.20	0.70	0.40	1.20	6.66		
Kure Beach (800-ft)	0.10	0.30	+0.30	0.22	4.45		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro		121 200	120 300	210 200	321 325		
Dallas		121 200	220 322	220 200	320 355		
Houston	020 200	• • •	121 333	220 333			
Anaheim	010 100	110 220	021 233	120 244			
Miami (inland)	010 100		010 222	120 233	321 335		
Miami (coastal)			031 333	121 244	321 255		
Newark	010 200		120 300	200 200	310 222		
Kure Beach (80-ft)	030 300		141 444	220 355	521 455		
Kure Beach (800-ft)	020 200		131 444	221 344	321 455		

TABLE A34b—Corrosion ratings for copper/1100 aluminum (aluminum skyward).

TABLE A34c-Mass loss (grams) for copper/1100 aluminum (copper skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.10	0.10	0.55	0.98	2.40		
Dallas	0.10	0.20	0.10	+0.51	2.11		
Houston	0	0.30	0.20	0.55	• • •		
Anaheim	0.10	0.10	+0.35	0.40			
Miami (inland)	0	0.20	0	0.21	0.29		
Miami (coastal)	0.10	0.20	+0.20	0.56	1.79		
Newark	0.10	0.20	0.50	1.41	4.10		
Kure Beach (80-ft)	0.20	0.40	+0.10	1.30	4.77		
Kure Beach (800-ft)	0	0.30	+0.40	+0.15	3.68		

TABLE A34d—Corrosion ratings for copper/1100 aluminum (copper skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 000	101 000	200 000	200 220	332 215		
Dallas	100 000	200 000	200 000	220 233	321 355		
Houston	100 000		200 000				
Anaheim	100 000	100 021	200 044	200 244			
Miami (inland)	100 000		201 022	200 233	321 334		
Miami (coastal)	100 000		201 033	201 244	311 255		
Newark	100 000		200 000	200 220	310 200		
Kure Beach (80-ft)	100 000		201 044	200 355	421 455		
Kure Beach (800-ft)	100 000		201 044	201 344	321 455		

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	0.30	0.20	0.50	0.45			
Dallas	0.10	0.40	+0.40	1.12	1.97		
Houston	0.30	0.80	0.20				
Anaheim	0	0.20	+0.80	1.08			
Miami (inland)	0.10	0.20	+1.00	+1.34	1.30		
Miami (coastal)	0	0.20	+1.30	0.33			
Newark	0.30	0.70	0.60	2.13	4.46		
Kure Beach (80-ft)		2.30	3.40	1.07	5.38		
Kure Beach (800-ft)	0.50	1.40	+0.10	0.47	••••		

TABLE A35a—Mass loss (grams) for copper/1100 aluminum/copper.

TABLE A35b—Corrosion ratings for copper/1100 aluminum/copper.

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	100 221	100 333	201 244	201 355	522 355		
Dallas	100 110	100 222	201 244	201 244	322 555		
Houston	100 222	101 233	201 244				
Anaheim	100 100	100 220	201 233	200 244			
Miami (inland)	100 110	101 232	201 244	201 355	302 455		
Miami (coastal)	101 222	101 233	201 255	201 355	413 455		
Newark	100 100	101 210	200 233	201 355	311 355		
Kure Beach (80-ft)		102 244	201 455	201 355	311 455		
Kure Beach (800-ft)	100 221	101 232	203 355	201 455			

TABLE A36a—Mass loss (grams) for copper/3003 aluminum/copper.

Site Attleboro Dallas	Exposure Time, Years						
	0.5	1.5	3.5	7,5	15		
Attleboro	0.30	0.40	0.80	0.50	1.36		
Dallas	0.20	0.40	0.80	+0.55			
Houston	0.20	0.40	1.30	• • •			
Anaheim	0	0.20	0.10	+0.95			
Miami (inland)	0.20	0.13	1.10	+2.29	3.84		
Miami (coastal)	0.20	0.53	1.00	+0.80	2.51		
Newark	0.20	0.68	1.50	1.68	1.08		
Kure Beach (80-ft)	0.60	0.93	+8.90	10.08	• • •		
Kure Beach (800-ft)	0.50	0.40	0.20	4.28			

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro	 	101 210	201 231	201 233	422 555		
Dallas	100 100	101 220	201 332	201 333			
Houston	100 110	101 220	201 433		• • •		
Anaheim	100 100	100 220	200 221	200 333			
Miami (inland)		101 230	201 332	202 443	302 544		
Miami (coastal)	100 200	102 220	201 321	201 342	241 544		
Newark	100 200	102 322	200 120	200 220	311 333		
Kure Beach (80-ft)		102 322	205 555	205 555			
Kure Beach (800-ft)		102 322	202 342	203 444			

TABLE A36b—Corrosion ratings for copper/3003 aluminum/copper.

TABLE A37a—Mass loss (grams) for copper/5052 aluminum (aluminum skyward).

Site	Exposure Time, Years						
	0.5	1.5	3.5	7.5	15		
Attleboro							
Dallas		0.20	0.33	0.50	1.23		
Houston		0	0.25				
Anaheim	0	0	0.10	0.31			
Miami (inland)	0.05	0	0.05	0.05	+0.84		
Miami (coastal)	0.20	+0.10	0.30	0.05	+1.11		
Newark	0.20						
Kure Beach (80-ft)	0.15	+0.50	0.70	0.85	+1.71		
Kure Beach (800-ft)	0.10	+0.50	0.16	0.55	+1.53		

TABLE A37b—Corrosion ratings for copper/5052 aluminum (aluminum skyward).

			Exposure Tim	e, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro					
Dallas	• • •	020 200	120 300	120 220	210 211
Houston		010 100	020 200		
Anaheim	010 000	020 120	020 220	120 220	
Miami (inland)	010 000	010 200	020 221	120 231	211 431
Miami (coastal)	010 000	010 100	020 211	120 231	220 333
Newark	010 000	•••			
Kure Beach (80-ft)	010 000	031 300	120 422	220 432	411 544
Kure Beach (800-ft)	010 000	020 311	120 422	120 332	323 444

			Exposure Tin	ne, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro					
Dallas		0.05	0.20	+0.03	0.93
Houston		0	0.25		
Anaheim	0	0	0.20	0.32	
Miami (inland)	0.10	+0.10	0.15	+0.38	+1.08
Miami (coastal)	0.20	+0.10	0.15	0.01	+0.33
Newark		+0.10	0.65	0.03	
Kure Beach (80-ft)	0.30	+1.2	1.05	0.05	+0.51
Kure Beach (800-ft)	0.25	+0.3	0.50	+0.47	+1.05

TABLE A37c—Mass loss (grams) for copper/5052 aluminum (copper skyward).

TABLE A37d—Corrosion ratings for copper/5052 aluminum (copper skyward).

			Exposure Tim	e, Years	
Site	0.5	1.5	3,5	7.5	15
Attleboro					
Dallas		200 000	200 000	200 130	210 222
Houston		200 000	100 010		• • •
Anaheim	100 110	202 010	200 031	200 131	
Miami (inland)	100 000	200 000	200 020	202 332	201 422
Miami (coastal)	100 000	200 000	200 010	200 332	210 433
Newark		200 000	200 010	200 100	
Kure Beach (80-ft)	100 000	200 010	200 022	200 442	211 544
Kure Beach (800-ft)	100 000	200 000	200 021	201 331	223 444

TABLE A38a-Mass loss (grams) for copper/5052 aluminum/copper.

-			Exposure Tim	e, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro	0.30	0.60	0.70	+0.20	
Dallas	0.10	0.20	0.80	+1.22	destroyed
Houston	0.10	0	+0.20	+0.29	• • •
Anaheim	0.10	0.20	+0.40	+2.29	
Miami (inland)	0.10	+0.30	+2.60	+7.61	+8.88
Miami (coastal)	0.30	0.30	+1.70	+6.45	+3.54
Newark	0.20	0.70	+1.10	+1.43	+2.97
Kure Beach (80-ft)	•••	0.70	+4.70		destroyed
Kure Beach (800-ft)	0.30	0.30	+2.30	+ 7.45	

			Exposure Tim	e, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro	 	101 321	201 321	201 344	423 544
Dallas	100 110	102 322	201 342	200 344	destroyed
Houston	101 221	101 322	202 344	201 344	
Anaheim	100 100	100 230	201 331	201 344	
Miami (inland)	101 110	101 221	201 342	201 354	311 555
Miami (coastal)	101 210	101 221	201 343	201 354	414 455
Newark	100 100	100 210	201 321	201 353	421 345
Kure Beach (80-ft)		102 333	202 454	201 555	destroyed
Kure Beach (800-ft)	101 210	101 232	202 454	201 454	414 555

 TABLE A38b—Corrosion ratings for copper/5052 aluminum/copper.

 TABLE A39a—Mass loss (grams) for lead/copper/5052 aluminum/copper/lead.

			Exposure Tin	ne, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro	0.10	0.30	1.05	2.39	1.91
Dallas	0.05	0.50	1.30	2.51	3.67
Houston	0.50	0.50	0.20	1.02	• • •
Anaheim	0.10	0.20	0	0.60	
Miami (inland)	0.20	0.20	0.25	0.27	1.80
Miami (coastal)	0.40	0.10	0.70	+0.83	3.38
Newark	0.10	0.30	0.40	1.10	3.56
Kure Beach (80-ft)	0.50	0.20	1.40	+2.21	
Kure Beach (800-ft)	0.60	0.50	1.80	+2.15	2.14

 TABLE A39b—Corrosion ratings for lead/copper/5052 aluminum/copper/lead.

			Exposure Tim	e, Years	
Site	0.5	1.5	3.5	7.5	15
Attleboro		200 100	200 100	201 200	442 411
Dallas	200 100	200 100	201 211	201 210	212 310
Houston	200 100		201 211	201 222	
Anaheim	200 100	200 100	100 100	200 100	
Miami (inland)	200 100		101 220	101 220	344 422
Miami (coastal)	200 100		201 321	201 331	445 444
Newark	200 100		200 100	200 100	311 200
Kure Beach (80-ft)	201 200		201 422	201 444	
Kure Beach (800-ft)	200 100		201 421	201 422	524 544

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Atmospheric Corrosion of Wrought Aluminum Alloys During a Ten-Year Period

REFERENCE: Dean, S. W. and Anthony, W. H., "Atmospheric Corrosion of Wrought Aluminum Alloys During a Ten-Year Period," Degradation of Metals in the Atmosphere, STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 191-205.

ABSTRACT: The deterioration in mechanical properties, mass loss, and the appearance of various forms of localized corrosion are documented for the exposure of a representative group of unstressed wrought aluminum alloys at three test sites over a ten-year period. Loss of ductility is the chief form of mechanical property damage observed. Among the forms of localized corrosion observed, intergranular corrosion, which led to partial sheet delamination or exfoliation, is the most damaging to the ductility of materials. Intergranular corrosion without a strong element of orientation in the wrought direction is less damaging, though more damaging than pitting without associated intergranular attack. A study of the effect of a sacrificial cladding layer indicated that loss of ductility can be completely eliminated when 7072 alloy is clad on 3004-H36 and 7178-T6 alloys, and 1230 alloy is clad on 2024-T3 alloy.

KEY WORDS: atmospheric corrosion, aluminum pitting, exfoliation, intergranular corrosion, clad aluminum, mechanical properties, tensile strength, elongation

Aluminum alloys are generally considered to have good resistance to corrosion in atmospheric exposure [1]. Uncoated aluminum alloys are used extensively in exterior applications for a variety of purposes, including structural, electrical conductor, thermal conductor, and architectural applications. A number of studies of the atmospheric corrosion behavior of aluminum alloys was carried out in the 1940s [2] and 1950s [3, 4], but recent studies have centered largely on stress corrosion resistance [5] and special applications [6].

This study [7] provides a compilation of the behavior of unstressed aluminum alloys under atmospheric conditions at different sites than previously studied. Atmospheric conditions in urban and industrial areas have undergone a substantial change in the past two decades due to environmental regulations. Recent results show that the rural atmosphere in the northeastern United States has become more corrosive to galvanized steel, while the industrial atmosphere surrounding New York City, for example, has become substantially less corrosive to galvanized steel [8]. It was of interest to see how aluminum alloys have responded to this change in the atmosphere. Unfortunately, this study was terminated after ten years so that the full impact of the environmental changes was never realized.

The present study also includes a full range of sheet materials in a range of tempers. Some limited extrusion alloys are also included. Some of the alloys in this study were not reported on previously.

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Materials Tested

Table 1 lists the alloy, alloying additions, temper, and form of the 27 materials tested. The specimens used for the outdoor exposure testing were chosen within a narrow gauge range (nominally 1.3 to 2.0 mm for sheet and approximately 3.0 mm for extruded material) so that strength and elongation loss values may be compared within the sheet and extrusion material categories, respectively. Table 2 lists the spectroscopic analyses of the bare alloys. Table 3 shows the spectroscopic analysis of the individual core and clad elements of the five sacrificial core clad combinations that were part of the study. All of the materials used were taken from contemporary commercially produced lots.

Test Procedures

Mill finish flat sheet products were sheared to 102 by 203 mm test specimens with the long edge in the rolling direction. Standard bus bar extrusions 102 mm wide were sheared to a 203 mm length. Identification numbers were stamped on each specimen and the specimens were solvent degreased and then cleaned in reagent nitric acid to remove any superficial oxide. The specimens were weighed to ± 0.01 g prior to exposure. The specimens were exposed in triplicate with removal planned for one, three, five, and ten years. Control specimens were retained in the laboratory to provide aged mechanical property data. This study presents only the results of the ten-year exposure, although the earlier results were examined to understand the behavior observed after ten years. Three exposure sites were chosen for this study: New Haven, CT; Brooklyn, NY; and Daytona Beach, FL. The exposures were initiated from 1963 to 1964.

New Haven, CT (NH) is a coastal urban-industrial environment. Test panels, racks, and stands were situated on the roof of a one story building. They faced in a southeasterly direction and were 45° from horizontal. The site was approximately 1.6-km north of New Haven harbor.

Brooklyn, NY (BR) is a severe industrial environment. Originally, the test panels were situated approximately 15 stories above land, just south of the Brooklyn bridge, 200 m from the East River, an estuary of varying salinity. In 1969, a new site was located about 3.2 km northeast of the former location, on the roof of a six-story building, approximately 420 m east of the East River and bordering the south bank of Newtown Creek in the Greenpoint section of Brooklyn. They faced in a southeasterly direction and were at an angle of 45° from horizontal at both Brooklyn sites.

Daytona Beach, FL (DB) represents a marine (high chloride containing) environment. Test panels, racks, and stands are situated on the ground 50 m from the mean high-tide water mark near the mouth of the Halifax River. Test panels faced in an easterly direction and were mounted 45° from horizontal. Positioned in this manner, the exposed surfaces of the test specimens were exposed to salt spray conditions (i.e., chloride contamination).

At the New Haven and Brooklyn sites, the specimens were held by aluminum bolts with neoprene rubber grommets to provide electrical insulation. It was necessary to replace the bolts and grommets used in long-term tests because of degradation of the rubber. Porcelain spools were used at Daytona Beach in accordance with the ASTM Standard Practice for Conducting Atmospheric Corrosion Tests on Metals (G 50).

Upon removal from the test site at each period, the panels were first examined visually and the condition noted. Corrosion products were removed in a mixture of chromic and phosphoric acids as recommended in ASTM Standard Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens (G 1). The acid mixture was prepared with reagent grade chemicals and distilled water. The cleaning solution contained 2% chromic acid (CrO₃) and 5% by volume ortho phosphoric acid and was maintained at 80° C. Test panels were immersed for 5 to 10 min and then rinsed in distilled water. They were then scrubbed with a sponge and rinsed again. If a film was still present, the panels were immersed in concentrated reagent grade nitric acid for 1 to 2 min and rinsed, scrubbed, and rinsed again in distilled water. This procedure was repeated until the samples were all free of corrosion products.

TABLE 1-Nomenclature of evaluated alloy systems.

Iloya Temper 0 0 0 0 0 0 0 0 116 0 116 55 0 113 55 0 13 55 13 13 55 14 13 55 13 55 55 14 13 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 14 14 55 15 14 55 16 14 55 17 55 55	in. 0.062 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.064 0.064 0.064 0.065 0.055 0.055 0.055 0.055 0.055 0.055 0.055 0.055 0.055 0.055 0.055 0.05	mm 1.57 1.57 1.60 1.60 1.60 1.60 1.63 1.63 1.63 1.63 1.63 1.63 1.65 1.65 1.65 1.65 1.65 1.65 1.65 1.65	Finish MFFS ⁶ MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFF	Additition(s) None None None None Mn, Mg Mg Mg Mg Mg Mg Mg
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A 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4	0.063 0.063 0.063 0.063 0.063 0.064 0.064 0.064 0.064 0.064 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.065 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.063 0.065 0.0550 0.0550 0.05500000000	1.57 1.60 1.60 1.60 1.60 1.63 1.63 1.63 1.63 1.63 1.63 1.65 1.65 1.65 1.65 1.65 1.65 1.65 1.65	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	None Cu, Man, Mg Cu, Mn, Mg Mn, Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg Mg M
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7 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	0.063 0.048 0.048 0.051 0.051 0.053 0.064 0.064 0.064 0.064 0.065	1.60 1.60 1.60 1.60 1.60 1.60 1.60 1.60	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Cu, Mn, Mg Cu, Mn, Mg Mn, Mn Mn, Mg Mn, Mg Mg Mg Mg Mg Mg Mg Mg Cr
74 4	0.063 0.064 0.051 0.051 0.051 0.064 0.064 0.064 0.064 0.064 0.065	1.60 1.22 1.22 1.60 1.63 1.65 1.63 1.65 1.65 1.65 1.65 1.65 1.65 1.65 1.65	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Cu, Mn, Mg Mn Mn Mn, Mg Mn, Mg Mg Mg Mg Mg Cr
A 4 4 A 4 CL H14 H14 H14 H36 H36 H36 H36 H36 H36 H36 H36	0.048 0.051 0.051 0.051 0.064 0.064 0.064 0.064 0.064 0.065	1.22 1.60 1.63 1.63 1.63 1.63 1.65 1.65	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Mn Mn, Mg Ma, Mg Mg Mg Mg Mg Mg Cr
H14 H24 H24 H24 H36 H36 H36 H36 H36 H36 H36 H36	0.063 0.051 0.051 0.064 0.064 0.064 0.064	1.60 1.60 1.63 1.63 1.63 1.63 1.63 1.63	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Mn Mn, Mg Ma, Mg Mg Mg Mg Mg Cr
A 4 H36	0.051 0.051 0.064 0.064 0.064	1.30 1.63 1.63 1.63 1.63 1.63 1.63	MFFS MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Mn, Mg Mn, Mg Mg Mg Mg Mg Mg Cr
A CL H36 55 H36 55 H36 75 H36	0.051 0.064 0.064 0.064 0.064	1.30 1.63 1.60 1.63 1.63 1.63 1.63	MFFS MFFS MFFS MFFS MFFS MFFS MFFS	Mn, Mg Mg Mg Mg Mg Cr
5 0 Shee 6 H36 Shee 6 H36 Shee 6 H36 Shee 136 H36 Shee 136 H36 Shee 136 H36 Shee 136 She	0.064 0.064 0.064 0.064 0.064	1.63 1.60 1.63 1.63 1.63	MFFS MFFS MFFS MFFS MFFS MFFS	M M M M M M M M M M M M M M M M M M M
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2 0 Shee 2 H16 Shee 6 H13 Shee 6 H33 Shee 6 H33 Shee	t 0.064 t 0.065	1.63 1.65	MFFS MFFS	Mg, Cr
2 H16 Shee 6 H16 Shee 6 H134 Shee 6 H136 Shee	t 0.065	1.65	MFFS	
6 0 Shee 6 H34 Shee 6 H36 Shee 6 H36 Shee	0.010			Mg, Cr
6 H34 Shee 6 H36 Shee 6 T5 E-14-16	1 0 0 0 0 0 0	1.2/	MFFS	Mg, Mn, Cr
6 H36 Shee	t 0.051	1.30	MFFS	Mg, Mn, Cr
Cutting	t 0.060	1.52	MFFS	Mg, Mn, Cr
	ion 0.117	2.97	As Extruded	Si, Mg
5 T42 Extrus	ion 0.116	2.95	As Extruded	Si, Mg
I T4 Shee	t 0.080	2.03	MFFS	Si, Mg, Cr, Cu
1 T6 Shee	it 0.064	1.63	MFFS	Si, Mg, Cr, Cu
A CL T4 Shee	t 0.064	1.63	MFFS	Si, Mg, Cr, Cu
3 T5 Extrus	ion 0.118	3.02	As Extruded	Si, Mg
5 T6 Shee	t 0.049	1.24	MFFS	Zn, Cu, Cr
5 CL T6 Shee	it 0.063	1.60	MFFS	Zn, Cu, Cr
8 CL T6 Shee	it 0.064	1.63	MFFS	Zn, Cu, Cr
iation Number. inish Flat Sheet. s evaluated.				
1 14 5.4 1 14 5.4 1 15 5.4 3 15 5.4 5 16 75 5.4 5 16 5.4 6 16 5.4 8 CL 76 5.4 8 CL 76 5.4 8 CL 76 5.4 6.4 16 5.4 16 5.4	t 0.080 t 0.064 t 0.064 t 0.064 t 0.063 t 0.063 t 0.063 t 0.063 t 0.063 t 0.063 t 0.063 t 0.064 b 0.050 t 0.050 t 0.050 t 0.051 t 0.055 t 0.055}t 0.055t 0	2.03 1.63 1.63 1.63 3.02 1.24 1.60 1.63 1.63 1.63 1.63 1.63 1.63 1.63 1.63	MFFS MFFS MFFS As Extruded MFFS MFFS MFFS Se.	4

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		,					Mass Pe	rcent*			
Alloy	Temper	Lot #	Si	Fe	Си	Mn	Mg	Cr	Zn	Ţi	Other
1100	0	27487	0.10	0.58	0.14	0.02	:	:	0.01	:	
1100	H16	397	0.06	0.57	0.14	0.01	:	:	0.01		
1100	H18	27486	0.06	0.71	0.11	0.01	:	:	0.10''	:	
2024	T3	27524	0.14	0.26	4.3	0.56	1.5	0.02	0.09	0.15"	0.2 Zr + Ti"
3003	0	27511	0.24	0.64	0.14	1.13	:	:	0.04	:	
3003	H14	27483	0.20	0.56	0.17	1.15	:	:	0.09	:	
3004	H36	27515	0.21	0.57	0.16	1.12	1.03	:	0.10	:	
5005	0	27489	0.08	0.45	0.03	0.02	0.74	0.01	0.01	÷	
5005	H36	394	0.05	0.44	0.04	0.01	0.83	0.01	0.01	:	
5050	0	27415	0.06	0.53	0.04	0.01	1.60	0.01	0.01	:	
5050	0	27520	0.09	0.56	0.05	0.02	1.30	0.01	0.02	:	
5050	H36	27417	0.13	0.49	0.06	0.03	1.55	0.02	0.07	:	
5050	H36	27513	0.12	0.48	0.03	0.03	1.53	0.01	0.02	:	
5052	0	27537	0.08	0.29	0.05	0.04	2.38	0.14^{h}	0.02	:	
5052	H16	27467	0.08	0.21	0.08	0.08	2.45	0.22	0.10	:	
5086	0	27516	0.10	0.32	0.08	0.44	3.7	0.12	0.02	0.02	
5086	H34	27507	0.10	0.33	0.09	0.44	3.9	0.14	0.04	0.02	
5086	H36	27416	0.01	0.39	0.10"	0.40	3.90	0.11	0.25"	0.02	0.02 Zr
6005	TS	27562	0.74	0.26	0.10"	0.01	0.56	0.01	$0.10^{"}$	0.01	0.01 Zr
6005	T42	27561	0.80	0.32	0.10"	0.01	0.61	0.01	0.10^{u}	0.01	0.01 Zr
6061	T4	27523	0.70	0.54	0.41°	0.08	0.98	0.20	0.04	0.02	0.02 Zr
6061	T6	27484	0.57	0.33	0.33	0.02	0.8-1.2"	0.20	0.01	0.02	
6063	TS	27564	0.48	0.17	0.05	0.02	0.62	0.01	0.13^{d}	0.01	
7075	T6	27508	0.13	0.38	1.9	0.08	2.2	0.21	5.9	0.03	0.01 Be
											$0.25 \mathrm{Zr} + \mathrm{Ti}^{\prime\prime}$
"Analvsis r	not available:	value chown	is maximum	n from <i>Rooi</i> e	tration Reco	rd of Alumin	um Associati	on Allov Des	vipnations an	d Chemical C	omposition Limits for

١. ò 5 Wrought Aluminum Alloys. The Aluminum Association, registration Accord of Atuminum W70% below the Aluminum Association registered range of 0.15 to 0.35. *7% below the Aluminum Association registered range of 0.15 to 0.35. *30% above the Aluminum Association registered limit of 0.10. *Aluminum content = remainder.

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TABLE 3

					-	Cladded Alloy:	s Mass F	Percent				
Alloy Temper	Core (Cladding)) Lot #	Si	Fe	Cu	Wn	Mg	Сr	μZ	Ц	Other	AI
CL 2024	2024	27536	0.50	0.50	3.8 to 4.9	0.30 to 0.9	1.2 to 1.8	0.10	0.25	0.15	0.20 Zr + Ti	Rem.
T3	(1230)	27536	0.7 Si +	· Fe	0.10	0.05	0.05	:	0.10	0.03	:	99.30 min
CL 3004	3004	27538	0.30	0.7	0.25	1.0 to 1.5	0.8 to 1.3	:	0.25	:	:	Rem.
H36	(7072)	27538	0.7 Si +	. Fe	0.10	0.10	0.10	:	0.8 to 1.3	:	:	Rem.
CL 6061	6061	27518	0.40 to 0.8	0.7	0.15 to 0.40	0.15	0.8 to 1.2	0.04 to 0.35	0.25	0.15	:	Rem.
Τ4	(7072)	27518	See Above	e Line								ł
CL 7075	7075	27519	0.40	0.50	1.2 to 2.0	0.30	2.1 to 2.9	0.18 to 0.35	5.1 to 6.1	0.20	0.25 Zr + Ti	Rem.
T6	(7072)	27519	See Above	s Line								ť
CL 7178	7178	27510	0.40	0.50	1.6 to 2.4	0.30	2.4 to 3.1	0.18 to 0.35	6.3 to 7.3	0.20	:	Kem.
T6	(7072)	27510	See Above	e Line								
"Analy	sis not avails	ahle: info	ormation extra	icted from	m Reoistrution	Record of Alu	minum Assoc	iation Allov De	esignations a	nd Chem	nical Composition	i Limits f
Wrought	Aluminum	Alloys,	The Aluminun	a Associa	tion, revised 1	June 1974.			0			

Mass loss measurements were made on the cleaned panels. Microscopic inspection was then carried out on the ten-year panels using a low power binocular microscope (7 to $\times 30$).

One specimen of each set of replicate panels removed was machined into a tensile specimen, and longitudinal mechanical properties were determined. Ultimate tensile strength, 0.2% offset yield strength, and percent elongation in 50.8 mm values were obtained. The crosshead speed was 42 μ m/sec to the yield point and 212 μ m/sec to fracture. The strength values were obtained according to ASTM Method of Tension Testing Wrought and Cast Aluminum and Magnesium Alloy Products (B 557). The strength loss values were calculated from these measured values by subtracting the values for the exposed samples from those of retained samples and expressing the loss as a percent of the retained sample values.

Pit depths were measured by a dial micrometer. Panels showing evidence of localized corrosion were sectioned and prepared for metallographic examination in the regions showing localized attack. Photomicrographs were made to show the morphology of localized corrosion.

Test Results

Mechanical Property Loss

Table 4 shows the percentage loss in longitudinal mechanical properties tabulated by alloy, temper, gauge, and form for exposure at New Haven, Brooklyn, and Daytona Beach test sites for a 10-year period. These data were sorted before tabulating to show the most severely damaged materials at the top of the table and the least damaged materials at the bottom of the table. The basis for this sorting process was the loss in ductility, which was by far the greatest form of damage to the mechanical properties.

Inspection of Table 4 shows that alloys such as 7075-T6, 2024-T3, 6005-T5, 6063-T5, represent the class of solution heat treatable and aged materials that suffered the most in loss of ductility. Among the nonheat treatable alloys, the most severely damaged materials were those where the greatest cold work had been introduced without partial annealing or stabilizing treatment. 1100 alloy in the H18 temper lost 22% of its ductility in Brooklyn, while the same alloy in the H16 and zero tempers lost 12% and 4.8%, respectively, in the same environment. A similar effect of cold work is shown in the comparison of 5052-H16 with 5052-0 in which the H16 material lost 7.5% of its ductility in Brooklyn and New Haven and lost almost none of its ductility in either environment in the zero temper.

The most striking result observed was the beneficial effect of cladding with sacrificial claddings of 1230 and 7072 alloys. For example, 2024-T3 lost 32% of its ductility in New Haven, while the same material clad with 1230 alloy lost no ductility in the same environment. Another example is 7075-T6, which lost 45.8% of its ductility in Brooklyn and lost only 2.5% when clad with 7072 sacrificial alloy. Other examples of protection from ductility loss resulting from the use of a 7072 alloy cladding layer occurred in 6061 and 7178, which showed no ductility loss with the 7072 cladding layer present. A partial exception to the beneficial effect of the 7072 cladding was 3004-H36, which lost 5% of its ductility in Daytona Beach. The sacrificial effect was, however, present in both New Haven and Brooklyn, where the sacrificial layer was completely effective in preventing ductility loss.

The loss in ultimate strength and yield strength was much less for most of the alloys tested than the ductility loss. The most severe loss occurred in the case of a 6005-T42 extrusion whose yield strength loss in Brooklyn exposure was almost 10%. Most of the other alloys, including those whose ductility dropped more than 20%, suffered strength losses in the 3 to 6% range. The clad materials generally had strength losses considerably less than the corresponding unclad materials.

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		č		Ultin	nate Strength	Loss	Yie	ld Strength I	SSO	Ш	ongation Los	S
		Cau	Ige	New		Davtona	New		Davtona	New		Davtona
Alloy	Temper	Inches	mm	Haven	Brooklyn	Beach	Haven	Brooklyn	Beach	Haven	Brooklyn	Beach
7075	T6	0.049	1.24	1.4	5.2	2.2	0.7	3.0	1.1	10	46	16
2024	T3	0.063	1.60	4.6	3.5	2.5	1.2	4.3	1.2	32	12	18
6005"	TS	0.117	2.97	1.0	5.0	2.9	0.5	4.3	1.6	18	28	23
6063"	TS	0.119	3.02	2.6	0	0	4.7	0	0	0	22	11
1100	H18	0.063	1.60	1.4	1.4	0	1.8	1.8	0.5	10	22	7
5086	H34	0.051	1.30	4.5	4.7	2.6	5.0	3.7	1.9	0	×	17
5086	H36	0.060	1.52	1.1	4.6	1.3	1.8	1.8	2.5	æ	14	7
6005"	T42	0.116	2.95	2.1	5.7	1.5	6.9	9.8	5.4	4	13	13
1100	H16	0.062	1.57	0	0	0	0	2.0	0.5	0	12	0
3003	H14	0.063	1.60	0	2.2	0	0	1.9	0	7	12	ę
5050/	H36	0.064	1.63	0.7	1.4	0.7	0.4	1.6	0.8	×	10	12
3003	0	0.048	1.22	0	2.4	1.2	1.4	1.4	1.4	1	12	4
3003	H36	0.051	1.30	0.8	3.1	1.0	0.9	4.1	2.6	4	12	12
5005	H36	0.063	1.60	2.6	2.8	0	2.6	1.1	0	6	11	2
6061	T6	0.064	1.63	1.1	3.1	0.6	2.4	4.4	1.5	1	2	10
5052	H16	0.065	1.65	2.0	3.0	1.2	1.8	2.6	1.2	œ	æ	0
5050*	0	0.064	1.63	1.1	3.7	0.9	0	2.1	1.0	e	S	0
3004 ^{h.c}	H36	0.051	1.30	0	0	0	0	1.4	0	0	0	S
6061	T4	0.080	2.03	3.0	5.0	2.7	4.7	7.4	7.1	e	S	0
11006.0	0	0.062	1.57	1.5	1.5	0	0	1.8	1.8	-	S	4
7075	T6	0.063	1.60	0	0.9	0	2.1	1.9	1.0	4	2	e
5005	0	0.064	1.63	0	1.7	0	0	0	0	0	1	0
5086	0	0.050	1.27	0	3.0	0	0.5	2.5	0.5	0	-	0
5052	0	0.064	1.63	0.3	1.4	0.3	0.8	0.8	0	0	1	0
6061 ^{h.c}	T4	0.064	1.63	1.5	3.2	1.0	2.8	2.1	0.7	0	0	0
71784.0	T6	0.064	1.63	0.2	1.0	0.6	0.9	1.0	1.3	0	0	0
2024 ^{b.d}	T3	0.063	1.60	0	0	1.3	0	0	1.4	0	0	0
"Extrusio	u											
"AIClad	CLUT 4											
"Clad wit	h 1230											
"Lot #275 /Lot #274	20											

Metallographic and Macrophotographic Examinations

The results of the macroscopic and metallographic examinations are categorized in Table 5. Photographic evidence supporting this formulation is presented in the following figures. Category 1 examples are illustrated in Figs. 1 and 2. Fig. 1 shows an example of highly directional intergranular corrosion in 2024-T3 sheet exposed in the skyward direction at Daytona Beach for five years. Fig. 2 shows exfoliation of the edge of a 7075-T6 sheet exposed in Daytona Beach for ten years. Shearing induced enough strain to cause exfoliation on the edges of these panels. The short transverse direction is most susceptible to exfoliation damage. Both 2024-T3 and 7075-T6 fall into the category of materials susceptible to severe loss of ductility on prolonged atmospheric exposure as noted in many earlier studies [4].

Category two materials show intermediate loss of ductility accompanied by intergranular corrosion with slight directionality. Category 2 examples are illustrated by Figs. 3 and 4, which show intergranular attack two to three grains deep in 6005 alloy resulting from exposure in Brooklyn and Daytona Beach, respectively, for a ten-year period. The severity of a ductility loss for 6005-T5 in a ten-year period is 13%, compared to losses of 32 to 46% for the Category 1 materials.

Category 3 materials show isolated pitting and moderate ductility loss. Fig. 5 shows an example of isolated pitting of 5052-0 after ten years of exposure in Brooklyn. The loss of ductility of this material was 0.8% or essentially zero.

Mode of Attack	Relative Severity of Ductility Loss	Loss of Elongation
Intergranular corrosion with greatest	most severe	>18%
involvement along grains parallel to the direction of deformation.	Category 1	
Intergranular corrosion with	less severe	between 18% and 5%
intermediate to slight preferred orientation.	Category 2	
Scattered pitting attack	least severe Category 3	<5%

TABLE 5-



FIG. 1–2024-T3, Daytona-5 yrs: Longitudinal Exfoliation. Skyward Surface, as polished, $100 \times$.



FIG. 2-7075-T6, Edge, Daytona-10 yrs: Severe delamination, 11×.



FIG. 3–6005-T5. Brooklyn-10 yrs: Intergranular Attack, two-three Grains deep. Skyward, Etch: Kellers-10 s 150S, Transverse.



FIG. 4–6005-T5, Daytona-10 yrs: Intergranular Attack, two-three Grains Deep, Skyward, Etch: Kellers-10 s 150×, Transverse.



FIG. 5-5052-0. Brooklyn-10 yrs: Pitting, Skyward Surface, 11×.

Mass Loss Due to Atmospheric Exposure

Table 6 shows the mass losses caused by corrosion on the materials exposed for the ten year period in New Haven, Brooklyn, and Daytona Beach. These data show a clear trend with respect to the relative severity of the test sites, with Brooklyn being most severe, followed by New Haven, with the least damaging site being Daytona Beach.

Specimens removed from the Brooklyn test site after ten years were generally dark gray from the deposition of black particulate matter embedded in the corrosion products. The source is believed to be soot and ash from combustion sources in the area.

Identical specimens removed from the New Haven test facility revealed corrosion products which were a lighter gray, indicating a lower content of particulate matter in that environment. Finally, identical panels removed from the Daytona Beach test site after ten years revealed frosty white corrosion products.

These data suggest that the carbonaceous particulate matter from the two industrial sites is a more potent agent for causing corrosion of aluminum alloys than the airborne salt coupled with high humidity at the Daytona Beach site. The presence of particles at discrete locations would also provide a mechanism for pit initiation. These particles are most likely fly ash from coal burning furnaces and carry heavy metals which are effective cathodes for local cell action.

Table 6, showing the mass loss data, is arranged in the same order going down the table as Table 4, in which the basis for order is decreasing ductility loss from the top of the table to the bottom. All three test sites show mass losses that have a very weak correlation to the loss of ductility shown in Table 4. For example, while the ductility loss of 7075-T6 is 46% and 2024-T3 clad with 1230 is zero in the Brooklyn site, the mass loss of 7075-T6 is 20.2 g/m² compared to 15.9 g/m² for 2024-T3 clad with 1230, a percentage difference of only 27%. The mass loss for the 2024 clad product is confined to the cladding in the form of flat bottom pits, so that there was no stress riser effect.

The rate of mass loss from all of these specimens is not linear with exposure time. In general, the mass loss rate decreases with exposure time in a manner similar to that observed for aluminum alloys [4] and for other metals in atmospheric exposures [9]. The following expression may be used to characterize mass loss as a function of exposure time:

$$M = Kt^n \tag{1}$$

		New 1	Haven	Broo	klyn	– Dayton	a Beach
Alloy	Temper	ML	PD	ML	PD	ML	PD
7075	T6	9.6	0.05	20.2	0.05	12.1	E
2024	T3	10.0	S	27.4	0.05		S
6005	T5	5.6	0.10	13.6	0.13	0	0.28
	extrusion						
6063	T5	5.2	0.05	12.6	0.10	1.2	0.30
	extrusion						
1100	H18	7.0	S	18.8	0.13	5.2	S
5086	H34	9.6	0.08	17.4	0.15	4.0	0.03
5086	H36	12.2	0.13	12.4*	0.13	5.6	0.13
6005	T42	6.2	0.13	13.0	0.18	2.4	0.18
	extrusion						
1100	H16			16.9*	0.05	5.0	0.08
3003	H14	8.2	S	24.8	0.05	7.2	S
5050	H36	6.2	0.03	15.2	0.08	4.0	0.03
3003	0	8.6	0.05	19.0	0.15	5.1	S
3003	H14	9.0	S	19.4	0.05	4.2	S
5005	H36			16.8*	0.18	4.1	0.18
6061	Τ6	7.0	0.03	15.4	0.15	6.0	0.05
5052	H16	7.3	0.03	18.1	0.03	3.0	S
5050	0	6.2	0.05	14.3	0.23	3.4	0.08
3004							
clad with 7072	H36	7.9	0.10	16.9	0.08	4.3	0.13
6061	T4	7.0	0.05	15.4	0.10	6.0	S
1100	0	7.4	S	15.4	0.05	4.7	0.08
7075	-						
clad with 7072	Т6	7.4	0.03	16.8	0.08	6.5	0.10
5005	0	6.0	0.10	14.4	0.15	2.8	0.15
5086	0	7.6	0.08	17.0	0.15	2.8	0.20
5052	Ö	6.9	0.05	15.4	0.25	2.9	0.03
6061	·	•••					
clad with 7072	Т4	7.0	0.05	16.0	0.10	7.1	S
7178					0110		
clad with 7072	Т6	6.6	S	11.8	0.13	4.2	0.05
2024	• •		~				
clad with 1230	Т3	6.6	S	15.9	S	4.4	S

TABLE 6-Mass loss and maximum pit depth caused by corrosion for a ten-year exposure period.

NOTE: ML = average mass loss in g/m^2 . PD = maximum pit depth in mm. S = less than 0.03 mm. E = exfoliation. * = 11.4 years exposure.

where M is the total mass loss caused by corrosion per unit of exposed area (g/m^2) ,

- t is the exposure time (years),
- K is a proportionality constant, and
- n is the mass loss exponent.

The K constant is the mass loss occurring in the first year of exposure and so is an indication of the initial rate of mass loss. The mass loss exponent n is a measure of the tendency for the corrosion process to accelerate or decrease with time. Values of n greater than one indicate an autocatalytic or accelerating corrosion process, while values less than one indicate a self-limiting process. Parabolic kinetics are seen when n is 0.5 and are typical of a system with a uniformly protective corrosion product layer.

To calculate the constants in Eq 1 from the mass loss versus time data, a logarithmic conversion is made. This linearizes the data so that a simple least squares regression analysis may be made. Replicate mass loss measurements are averaged and the mean mass loss values are used in the regression analysis. Correlation coefficients are calculated to show how good the data fit. In general, the closer the correlation coefficient R is to one, the better the fit. The calculated values of K, n, and R are given in Table 7.

The values for the New Haven site are of substantially poorer accuracy because many of the early samples were not removed or were lost. The values for n, the mass loss exponent, tend to be greatest at the Brooklyn site. Also the mass loss exponents are greater for clad alloys, probably because the metal loss occurs mainly in the cladding, and exposure of the core alloy tends to accelerate the corrosion of the cladding.

Discussion

It is of interest to compare the results of this study to earlier results. The ASTM B 3-1957 [10] program included many of the alloys covered in the present study. The seven-year results are

]	Brooklyn	l	N	ew Have	n	Day	ytona Be	ach
Alloy	Temper	n	К	R	n	К	R	n	К	R
1100	0	0.78	2.7	0.99	0.30	3.3	0.83	0.27	1.7	0.43
1100	H16	0.52	5.4	0.88	0.66	1.9	1.00	0.65	1.1	0.99
1100	H18	0.71	3.3	0.98	0.31	3.0	0.84	0.25	1.9	0.38
2024	Т3	0.66	6.8	0.97	0.29	4.7	0.84	0.19	6.2	0.42
2024 CD	Т3	1.18	1.2	0.99	0.35	2.4	0.71	0.67	0.9	0.98
3003	0	0.88	2.8	0.98	0.43	2.5	0.72	0.51	1.4	0.98
3003	H14	0.78	4.3	0.99	0.26	3.6	0.44	0.59	1.8	0.95
3004	H36	0.90	2.7	0.98	0.46	3.3	0.93	0.77	0.8	0.97
3004 CL	H36	0.88	2.2	0.99	0.86	0.6	0.60	0.62	1.0	0.99
5005	0	1.10	1.3	0.98	0.35	2.1	0.88	1.41	0.1	0.91
5005	H36	0.45	4.9	0.78	0.66	1.9	0.99	0.48	1.7	0.86
5050°	0	0.50	5.6	0.81	0.58	1.9	0.99	0.69	0.9	0.96
5050 ^d	0	1.04	1.6	0.96	1.45	0.3	0.79	1.39	0.2	0.77
5050°	H36	0.21	7.6	0.33	0.78	1.6	0.91	0.76	0.9	0.98
5050/	H36	0.92	2.1	0.98	0.40	1.9	0.71	0.97	0.6	0.87
5052	0	1.02	1.8	0.98	0.36	2.5	0.70	0.59	0.8	0.93
5052	H16	0.60	4.3	0.99	0.31	3.0	0.75	0.53	1.0	0.97
5086	0	0,94	1.6	0.87	0.31	3.2	0.74	1.00	3.6	u
5086	H34	0.91	2.7	0.95	0.33	3.9	0.81	0.71	0.9	0.85
5086	H36	0.38	6.3	0.82	0.81	2.7	0.92	0.62	1.4	0.80
6005 Ext	T5	0.58	3.4	0.94	1.95	0.05	0.93			ь
6005 Ext	T42	0.69	2.5	0.96	1.38	0.2	0.98	1.77	0.03	0,80
6063 Ext	T5	0.73	2.3	0.99	0.89	0.6	0.91	1.54	0,06	0.83
6061	T4	0.67	3.8	0.98	0.77	1.3	0.82	1.06	0.8	0.84
6061	T6	0.65	4.5	1.00	0.33	2.9	0.62	0.61	1.3	0.99
6061 CL	T4	0.82	2.7	0.99	0.43	2.0	0.70	0.73	1.4	0.98
7075	T6	0.82	3.9	0.91	0.34	4.0	0.50	0.82	2.3	0.93
7075 CL	T6	1.22	1.3	0.98	1.65	0.2	0.81	0.95	0.7	0.76
7178 CL	Т6	1.01	1.5	0.98	1.41	0.3	0.96	0.70	0.8	0.94

TABLE 7-Mass loss versus exposure time regression analysis results.

"Based on only two points.

^bInsufficient data to make analysis.

°Lot #27415.

^dLot #27520.

"Lot #27417.

/Lot #27513.

NOTE: CD = AlClad with 1230. CL = AlClad with 7072. $M = Kt^n$, m = mass loss in g/m², t in years. K = regression coefficient to give mass loss in g/m². n = mass loss exponent on years exposure.

roughly comparable and it is instructive to compare the mass loss values for these two exposures. Some of these values are presented in Table 8. It is apparent that the Daytona Beach site is less severe than the Kure Beach 25-m site. This is to be expected, because the Daytona Beach site is significantly further from the mean high tide point, so that the ocean spray has further to travel to reach the specimens.

The Newark-Kearney mass loss results fall between the Brooklyn and New Haven mass loss results. This again is more or less what would be expected from the proximity to local sources of fly ash and other particulates. Unfortunately, we are not able to draw any conclusions on changes in the atmosphere because of the relatively short exposure, except to note that the Brooklyn site is certainly aggressive to the aluminum alloys studied during this period. It will be of interest to compare results from more recent studies, such as the 1976 G 1 program [11], to see if the atmosphere in urban sites becomes less aggressive to uncoated aluminum alloys as a result of regulations designed to minimize atmospheric pollution.

The mass loss regression data is of interest because this approach to reporting aluminum mass loss data has not been widely reported. In many sources, atmospheric corrosion is reported as a linear rate. However, extrapolation of corrosion caused mass loss is much more likely to be accurate if the proper correlation equations are used. In general, when localized corrosion processes dominate, the mass loss exponents will be significantly less than one. This is a result of increasing diffusion lengths and the presence of corrosion product films. However, it should be noted that mass loss does not necessarily correlate well with the extent of damage caused by localized corrosion. For example, the mass loss values were generally less at Daytona Beach, but the pit depths were often greater.

It is also significant that the pitting found on the skyward side of the panels was greater, both in depth and frequency, than on the groundward side. This was observed on specimens from both New Haven and Brooklyn. At Daytona Beach the groundward pitting was about equivalent to the skyward side. This is of interest because it has been observed in other studies that pitting on aluminum panels on the groundward side is more severe than on the skyward side [4]. The reason for this difference in behavior is probably related to the aggravating effect of particulate fallout, especially in industrial sites. It may also be related to the fact that the referenced studies used a 30° exposure angle rather than the 45° angle employed in this study.

The loss of ductility is of interest because it correlates far better with the development of intergranular corrosion than with mass loss. The results on 6005-T5 show this clearly. This alloy has very small measured mass loss values, but the pitting is intergranular in nature and the alloy suffered substantial loss in ductility. The presence of intergranular attack apparently serves as stress risers during the mechanical testing and caused crack propagation. The presence of chlorides in the atmosphere apparently aggravates the tendency towards intergranular corrosion,

				Mass Loss			
		Mai			Industrial		
		КВ	DB	NK	ВК	NH	
Alloy	Temper	Seven Years	Ten Years	Seven Years	Ten Years	Ten Years	
1100	u	5.8	5.0	7.2	18.8	7.0	
3003	H14	5.6	7.2	12.0	24.8	8.2	
5005	H34	6.3	4.1				

TABLE 8-Comparison of selected mass loss values with ASTM B3-57 exposure results.

"1100 panels were H14 temper at KB and NK sites; H16 temper at DB, BK and NH sites. *NOTE*: All mass loss values in g/m^2 . KB = Kure Beach 25-m lot. DB = Daytona Beach 50-m lot. NK = Newark-Kearney. BK = Brooklyn. NH = New Haven. especially in pits. It was surprising to see the number of alloys which exhibited intergranular corrosion associated with pitting. Cold work in alloys also seems to aggravate the intergranular corrosion process.

On the other hand, the ability of the alclad alloys to resist damaging localized attack was apparent. The cladding clearly prevented intergranular attack of the basis alloy and so these alloys showed no loss in ductility, even though the mass loss rate was appreciable. Thus, the concept of using clad alloys to maximize the load carrying capacity of aluminum alloys seems justified.

Conclusion

The main conclusions to be drawn from the corrosion data are as follows:

1. A sooty industrial environment is far more damaging to unstressed aluminum alloy than a warm, humid, salt-laden seacoast atmosphere from the standpoint of general mass loss.

2. By far the most noticeable effect of prolonged atmospheric exposure is loss of ductility in susceptible alloys, which correlates with a tendency toward exfoliation corrosion. Intergranular corrosion without a special orientation in the direction of the process deformation is far less damaging to ductility and isolated pitting corrosion has almost no damaging effect on ductility.

3. Materials in tempers which maximize their mechanical strength suffer the greatest loss in ductility.

4. Sacrificial cladding, particularly of materials in tempers which maximize their mechanical strength, completely eliminates ductility loss.

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Barrier Coatings for the Protection of Steel and Aluminum Alloys in the Marine Atmosphere

REFERENCE: Shaw, B. A. and Aylor, D. M., "Barrier Coatings for the Protection of Steel and Aluminum Alloys in the Marine Atmosphere," *Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 206-219.

ABSTRACT: The marine atmospheric corrosion resistance of a variety of metallic, ceramic, and metallic/ceramic coatings on aluminum and steel alloys is investigated to assess the long term protection capabilities of these barrier coatings. Results of 6 to 42 month exposures indicate that the following coatings provide the best marine atmospheric corrosion protection: thermal sprayed aluminum, zinc, zinc-aluminum pseudo alloy, aluminum oxide (Al₂O₃), and both zinc-based and aluminum-based metallic/ceramic coatings. The application of a low viscosity sealer to one of the ceramic coatings extends the protective capability of the coating.

KEY WORDS: coatings, metallic coatings, metallic/ceramic coatings, ceramic coatings, thermal spray, flame spray, arc spray, plasma spray, electron probe microanalysis, metallography, corrosion, aluminum, zinc, zinc-aluminum alloys, marine exposures, marine atmosphere, steel

Increasing use of aluminum and steel structural alloys in the marine atmosphere necessitates the development of corrosion coating technology to extend the service life of these materials. Metallic, ceramic, and metallic/ceramic barrier coatings have shown promising corrosion performance in marine atmospheric environments and, therefore, were chosen for evaluation [1-8]. The protection provided by these coatings ranges from strictly a physical barrier (ceramic) to a physical barrier plus some degree of sacrificial protection (metallic and metallic/ ceramic). The specific objective of this research is to assess the long-term protection capabilities of these barrier coatings. Service life predictions are discussed as well as corrosion mechanisms for selected coatings.

Coatings

Listings of the types of coatings evaluated in this investigation are presented in Tables 1 to 3. A variety of methods were used to apply the metallic, ceramic, and metallic/ceramic coatings. Six out of the eight metallic coatings and both of the ceramic coatings were applied using thermal spray processes. Aluminum coatings deposited by room temperature peen plating and by electroplating were also evaluated. The metallic/ceramic coatings were applied by either a room-temperature hand-spraying process or through the use of a dip/spin technique.

In the thermal spray process, the coating material (in the form of wire, rod, cord, or powder) is melted by either a gas flame or electrical heating. After melting, the material is accelerated

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coatings.
-Metallic
TABLE 1

Preparat	e on Coating Composition	Thickness µm	Method of Application	Number of Specimens
	varied from 85% Zn/15% Al to 40% Zn/60% Al by weight	175 to 250	Arc Sprayed	٢
	approximately 85% Zn-15% Al	175 to 250	Flame Sprayed	٢
	top layer 99.5% Zn bottom layer 99.0% Al	175 to 250	Flame Sprayed	7
	top layer 99.0% Al bottom layer 99.5% Zn	175 to 250	Flame Sprayed	7
	99.0% Pure Al	175 to 250	Flame Sprayed Arc Sprayed	0 v.
	99.5% Pure Zn	175 to 250	Flame Sprayed Arc Sprayed	2 °
	99.5% Al-50% glass 50% (average) fragments	50 to 125	Room temperature Peen Plating	15
	99.99% AI	25	Low temperature Electroplating	4

NOTE: 1 = degrease, initial grit blasting to clean surface, final grit blasting with Al₂O₃ (mesh 16-30) to obtain a white metal surface with surface profile of 50 to 75 μ m (Ref 12), 2 = polish to 600 grit finish, and 3 = anodically cleaned in Oakite 90 (alkaline cleaning solution containing sodium hydroxide and sodium "2 panels from supplier number one, 3 from supplier number two.

carbonate) to remove grease and 10% HCl acid dip to remove oxides and corrosion products.
Coating Designation	Substrate Material"	Coating	Coating Thickness (µm) [*]	Bond Coat	Sealer	Number of Specimens
	 ↑	·				
1	5086-0 and	99.5% Al ₂ O ₃	Î	None	None	12
J	6061-T6	99.5% Al ₂ O ₃	 125-	89.5 Ni-5.5 Al-5 Mo	None	15
К	Al	87% Al ₂ O ₃ -13% TiO ₂	200	89.5 Ni-5.5 Al-5 Mo	None	9
L	Ļ	87% Al ₂ O ₃ -13% TiO ₂	Ļ	89.5 Ni-5.5 Al-5 Mo	Phenolic	9

TABLE 2—Ceramic coatings.

"Surface preparation was the same as that for the thermal sprayed metallic coatings (Table 1, Substrate Preparation Procedure 1).

"Excluding bond coat.

Coating Designation	Coating Composition	Method of Application	Number of Specimens
М	Zinc Base with Potassium Silicate Binder	Hand Sprayed, Air Cured	9
Ν	Zinc Base with Potassium Silicate Binder	Dip/Spin Applied, Air Cured	9
0	Aluminum Base with Phosphate/Chromate Binder and Inorganic Topcoat	Hand Sprayed, Oven Cured	9
Р	Aluminum Base with Phosphate/Chromate Binder and Fluorocarbon-modified Silicone Topcoat	Hand Sprayed, Oven Cured	9
Q	Aluminum Base with Phosphate/Chromate Binder and Fluorocarbon-modified Silicone Topcoat	Dip/Spin Applied, Oven Cured	9
R	Aluminum Base with Phos- phate/Dichromate Binder and Ceramic Sealer	Hand Sprayed, Oven Cured	9

TADI	EC	> > > > > > > > > > > > > > > > > > > >	atalli	-/	a contra	an atiman
IADI		M	eiuiii	c/cer	amic	couings.

Note: Coatings were applied onto carbon steel fasteners. Surface preparation consisted of degreasing the fasteners and grit blasting with 100-grit Al_2O_3 . Coating thicknesses were 25 to 50 μ m.

toward the grit blasted substrate surface, where it impacts and solidifies to form a layered coating. Three types of thermal spray processes were used to deposit the coatings investigated in this evaluation: flame spraying, arc spraying, and plasma spraying. Flame spraying uses the heat from a chemical reaction to melt the coating material—typically an oxygen-acetylene fuel gas mixture is used. A jet of compressed gas, usually air, is used to accelerate the molten droplets toward the substrate. Materials that melt at temperatures less than 2760°C without sublimation are capable of being applied by this process. Coating materials requiring higher melting temperatures use electrical heating for melting.

In the arc spray process, the coating material, in the form of wire or rod, is melted when a potential difference is applied across the two consumable wire electrodes. A stream of com-

pressed gas is directed across the arc zone, shearing off the molten droplets and projecting them towards the substrate. Materials with melting temperatures of 4000°C or less can be applied using the arc spray process. Coating materials with melting temperatures over 4000°C can be melted using a plasma (ionized gas) heat source. Plasma spraying is typically used to apply oxide and carbide coatings for high-temperature corrosion and wear applications. Several detailed treatments of thermal spray coating processes are available in the literature [9-11].

The "as deposited" structure of a thermal spray coating is different from that of the same material in wrought form due to the incremental nature of the coating buildup and the fact that coating composition is affected by reaction of the coating material with process gases and the atmosphere. The as-applied structure of all thermal spray coatings is similar in layered structure and in that they all contain some degree of porosity. Figure 1 presents a schematic crosssection of a thermal spray coating showing parameters that influence coating structure.

Eight metallic thermal spray coatings were evaluated. The coatings were sprayed in accordance with DOD-Std 2138(SH), Nov. 1981 [12] to a thickness of 175 to 250 μ m. Low-carbon steel substrates were used for all of the metallic thermal spray coatings. Panel dimensions before spraying were $4 \times 6 \times 1/8$ in. ($10.2 \times 15.2 \times 0.32$ cm), and each panel was coated on both sides and all four edges. Initial substrate preparation consisted of degreasing and abrasive blast cleaning of the panels. Final surface preparation involved abrasive blasting of the panels with aluminum oxide (mesh size 16-30) to obtain a white metal surface with an anchor tooth profile of 50 to 75 μ m. All of the coatings were evaluated in the "as-sprayed" condition, with scribe marks extending to the base metal on several of the specimens. The "as-sprayed" or unsealed condition represents a "worst possible case" type of exposure, since these coatings are typically sprayed or brushed with a low-viscosity sealer prior to use.

Coating A was arc sprayed using two different consumable wire electrodes, one aluminum, the other zinc. The diameters of the two consumable wire electrodes were chosen to produce an approximate coating composition of 85% Zn/15% Al. The actual composition of coating A varied between 15% Al/85% Zn and 60% Al/40% Zn by weight. Coatings C and D were obtained by flame spraying one material to a coating thickness of 100 μ m, and then spraying the second material over the top of the first to obtain a total coating thickness of approximately 200 μ m. Variations in thickness of 50 to 75 μ m were common for the flame sprayed coatings, and variations of 50 to 125 μ m were common for the arc sprayed coatings. Typical porosity levels for the flame and arc sprayed coatings ranged from 5 to 15% by volume.

In addition to the thermally sprayed coatings, peen sprayed aluminum and electroplated aluminum coatings were also evaluated. Coating G was obtained by spraying an aluminum powder (99.5% Al) glass bead mixture at room temperature onto 5086 aluminum panels. Substrate preparation consisted of polishing the "as-received" surfaces of the panels with 600 grit paper



FIG. 1-Schematic cross section of a thermal spray coating.

before application of the coating. The coatings were applied to both faces of $3 \times 4 \times \frac{1}{8}$ in. $(7.6 \times 10.2 \times 0.32 \text{ cm})$ panels to a coating thickness of 50-125 μ m. Epoxy was used to seal the uncoated panel edges prior to exposure. Again, the coated panels were exposed in the "as-deposited" condition. Coating H was obtained by electroplating aluminum from a nonaqueous organic electrolyte. The proprietary deposition process very similar to the process developed by Ziegler [13], operates at a relatively low temperature (100 to 120°C), and no hydrogen in the ionic state is present or can be produced by decomposition reactions. The electroplated coatings were applied to a thickness of 25 μ m and were evaluated in the "as-deposited" condition. Panel dimensions were $4 \times 6 \times \frac{1}{32}$ in. (10.2 \times 15.2 \times 0.32 cm) before coating and the edges were sealed with epoxy before exposure.

Two ceramic coatings were evaluated on both 6061-T6 Al and 5086-0 Al panels. The coatings were plasma sprayed on both faces and each of the four edges of $3 \times 4 \times 1/8$ in. $(7.6 \times 1.0 \times 0.3 \text{ mm})$ panels. Substrate surfaces were prepared in the same manner as described above for the metallic thermal spray panels. Coating J was prepared using a 89.5% Ni/5.5% Al/5% Mo bond coat (75 μ m thick) under the aluminum oxide. This was done to determine whether the bond coat improved coating adhesion to the substrate. Both coatings K and L contained a bond coat. Coating thicknesses (excluding bond coat thickness) ranged from 125 to 200 μ m. Coating L contained a brushed-on phenolic sealer.

All of the metallic/ceramic coatings evaluated were applied to carbon steel fasteners of size 0.5 in.-13 UNC by 1 in. long. All fasteners were prepared for coating by degreasing followed by grit blasting with 100 grit aluminum oxide (mesh size). Coatings were then applied by conventional, air-assisted hand spraying or by dipping a 11.34 kg (25 lb) batch of fasteners into the coating material and then spinning to remove any excess coating. Two basecoats were deposited and one topcoat, where required. Final coating thicknesses averaged 25 to 50 μ m. Coatings requiring oven curing were baked for 1 h at 650°F (343°C) after applying each coat.

Experimental Procedure

All of the specimens were exposed at the LaQue Center for Corrosion Technology's marine atmospheric test site in Kure Beach, NC for exposure periods ranging from 6 to 42 months. Table 4 lists the exact exposure times. The specimens were exposed on racks located 25 m (80 ft) from the ocean and angled 30° from horizontal, facing the ocean. Metallographic analysis and/ or electron probe microanalysis was used to characterize the coatings before and after corrosion exposure.

Results and Discussion

Marine atmospheric observations of all coatings evaluated are listed in Tables 4 to 6.

Metallic Coatings

After 34 months of marine atmospheric exposure, coating A was in good condition. A light deposit of zinc and aluminum corrosion products was noted on each of the seven specimens examined. No blistering of the thermal spray coating and no corrosion of the steel substrate was observed. Metallographic examination of the coating revealed widespread depletion of zinc from the zinc-rich areas within the coating (Fig. 2B). Previous characterization [14] of the pseudo-alloy coating has shown the coating structure to be lamellar, with very distinct zinc-rich (>90% Zn) and aluminum-rich (>90% Al) areas (Fig. 2A). Electron probe microanalysis of thermal spray coatings after exposure has shown that the oxide layers and pores within the coating form a continuous path for the ingression of chlorides into the coating. Corrosion of the coating layers. Severe mechanical degradation of the coating is anticipated in the future due to the continued depletion of zinc from the zinc-rich areas.

Coating Designation	Exposure Time, months	Appearance			
A	34	Light accumulation of zinc-aluminum corrosion products on coating surface. Metallographic analysis revealed widespread depletion of zinc from zinc-rich areas within the coating.			
В	34	Blisters noted within the coating and not at the coating-substrate inter- face. Metallographic/microprobe analysis indicates depletion of zinc-rich phase along oxide layers within coating.			
С	34	Heavy accumulation of zinc corrosion products. In some locations zinc layer totally depleted.			
D	34	Dark (Black) staining of coating. Blistering between zinc and alumi- num layers noted on 4 of 7 specimens.			
E	42	Supplier #1 Light accumulation of Al corrosion products, Supplier #2 Relatively large blisters (10 mm in dia) noted at coating—substrate interface.			
F	42	Heavy accumulation of zinc corrosion products.			
G	6	Severe flaking/spalling of the coating. Metallographic examination re- vealed large amounts of fragmented glass within the coating.			
н	6	Blistering/delamination of the coating at the coating-substrate inter- face.			

 TABLE 4—Corrosion performance of metallic coatings.

 TABLE 5—Corrosion performance of ceramic coatings.

Coating	Exposure Time, months	Appearance			
I	18	Blistering of coating, exposing underlying substrate within four months' exposure. Minimal increased corrosion between 4 and 18 months.			
J	24	Grey stain present on all coated panel surfaces.			
К	18	Blistering of coating noted after four months' exposure. Blistering ex- tensive enough to expose substrate noted after 9 months', with in- creasing corrosion through 18 months.			
L	18	Blistering of coating noted after nine months' exposure. Exposure of substrate from blistering was found in some areas after nine months, but the extent of corrosion was much less severe than that on un- sealed Al ₂ O ₃ -TiO ₂ panels after nine months. The corrosion of the sealed panels increased between 9 and 18 months.			

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Coating	Exposure Time, months	Appearance			
М	31	White corrosion products on all fasteners. Slight pinhole rust on 2/9 nuts noted after 25 months' exposure.			
N	24	25% base metal rust noted on $1/6$ fasteners after three months' exposure. Up to 20% base metal rust noted on remaining $5/6$ fasteners after nine months' exposure.			
0	31	White corrosion products on all fasteners. Slight pinhole rust on 4/9 fas- teners noted after seven months' exposure.			
Р	31	Slight pinhole rust.			
Q	31	Moderate pinhole rust.			
R	30	Moderate pinhole rust.			



FIG. 2—Arc-sprayed zinc-aluminum pseudo alloy coating (unetched).

Coating B changed in color from a metallic silver grey to a dark charcoal grey after exposure. Flaking and blisters of the thermal sprayed coating was noted on each of the seven specimens, with blisters averaging 5 mm in diameter. Despite the poor condition of the coating, it was still able to completely protect the base metal. Metallographic examination of the coating showed extensive depletion of zinc from the zinc-rich phase along the oxide layers within the coating (Fig. 3). Previous characterization [14] of the prealloyed wire coating has shown a structure comprised of a very fine dispersion of zinc-rich and aluminum-rich phases. X-ray area scans of a coating cross-section before exposure are presented in Fig. 4 and show the uniform distribution of zinc, aluminum, and oxygen within the coating. Degradation of the coating along the oxide layers and pores. An aluminum-rich matrix is left behind after the zinc is depleted, but this matrix is weak and eventually collapses, resulting in the formation of large voids within the coating.

Coating C displayed heavy zinc corrosion product formation on the bottom half of each of the seven panels after exposure. No blistering of the coating and no base metal corrosion were noted on any of these panels. Optical cross sections of the coating revealed moderate to heavy corro-



FIG. 3-Flame-sprayed zinc-aluminum prealloyed wire coating (unetched).

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FIG. 4—X-ray area scans for zinc-aluminum pralloyed wire coating cross section.

sion of the zinc layer (Fig. 5). Longer exposures will be necessary to determine whether the duplex zinc-top coatings show improved long-term performance over pure zinc coatings. Visual examination of coating D showed small blisters on four of the seven specimens and dark staining indicative of the initiation of base metal corrosion on each of the panels.

After 42 months of marine atmospheric exposure, three of the five flame-sprayed coating E specimens and both of the arc-sprayed coating E specimens were in very good condition. Little corrosion product build-up and no blistering of the coating were noted on these five specimens. No evidence of base metal corrosion was found on these five specimens, but it should be noted that none of the specimens were scribed. It is expected that a light buildup of rust would have been formed along the scribe if the panels had been scribed. Optical cross-sections after exposure show slight degradation of the coating initiating along the oxide layers and adjacent to pores in the coating (Fig. 6). Two of the five thermal sprayed coating E panels exhibited blistering of 10% of the coating along the panel edges. Both of these specimens and one of the good specimens were prepared by a second supplier. Blister sizes ranged from a couple of millimeters in diameter to >10 mm in diameter. The blisters formed along the coating substrate interface and contained large amounts of aluminum corrosion product. No rusting of the base metal underneath the blisters was noted on the specimen removed for detailed evaluation. These early failures have been attributed to either improper coating application or insufficient surface prep-



FIG. 5—Flame-sprayed duplex zinc-top coating (unetched).



FIG. 6-Flame-sprayed aluminum coating (unetched).

aration by the second supplier, and emphasize the critical nature of these two steps in the overall long-term performance of the coating.

The five flame-sprayed and two arc-sprayed coating F panels exhibited moderate to heavy zinc corrosion product buildup after 42 months of atmospheric exposure. No blistering of the coating and no base metal corrosion were observed. Metallographic examination of the coating showed widespread depletion of zinc along the oxide layers and a heavy buildup of zinc corrosion products at the coating surface (Fig. 7).

Severe degradation of coating G was observed after six months of exposure, (Fig. 8B). Characterization of the coating before exposure revealed a large amount of fragmented glass within the coating, (approximately 50% by volume) (Fig. 8A). Degradation of the coating resulted from the ingression of chlorides along the paths provided by the fragmented glass.

After six months of exposure, coating H exhibited light staining and blistering/delamination of the coating (Fig. 9). Characterization of the coating prior to exposure revealed a very dense coating of uniform thickness with some delamination of the coating noted. No base metal corrosion was detected beneath the coating, but rust was noted in areas where the coating had been intentionally damaged.



FIG. 7-Flame-sprayed zinc coating (unetched).

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FIG. 8-Peen plated aluminum coating (unetched).



FIG. 9-Electroplated aluminum coating after six months' marine atmospheric exposure.

Ceramic Coatings

Coatings I and J exhibited varied results independent of the substrate material. The panels containing a nickel bond coat under the ceramic coating exhibited blistering extensive enough to expose the substrate within four months' atmospheric exposure (Fig. 10). Minimal increased corrosion was noted between 4 and 18 months. In contrast, panels prepared at a separate site



FIG. 10-5086 Al panel with Al₂O₃ plasma spray coating after four months' marine atmospheric exposure.

with no bond coat remained in excellent condition after 24 months' exposure. The only evidence of coating deterioration was the presence of a grey stain on the panel surfaces. These variations in coating performance are presumably due to differences in the quality of coating application at the two sites at which the panels were prepared, not to the nickel bond coat.

The corrosion resistance of coatings K and L was below that of coatings I and J. Blistering of coating K was noted after four months, with increasing corrosion through 18 months. Blistering of coating L (the same as coating K, but sealed) did not occur until nine months, and the extent of corrosion was significantly less severe than on the unsealed panels. However, the corrosion performance of the sealed panels was still well below an acceptable level. The condition of coatings K and L after 18 months' exposure is seen in Fig. 11.

The rapid blistering noted above suggests inadequate coating adherence. A lack of coating adhesion was identified in a few areas on both of the ceramic coated panels before marine exposure, which would be obvious sites for increased coating degradation and eventual substrate corrosion upon exposure. Examination of the ceramic coatings after marine exposure identified coating deterioration at both the ceramic coating/bond coating interface as well as at the bond coating/substrate interface. Figure 12 exemplifies a typical coating defect before exposure as well as coating disbondment at both ceramic coating/bond coating and bond coating/substrate interfaces after marine exposure. These findings suggest that neither the bond coating application. Improper application of the plasma spray coating can result in very early failure, whereas a properly applied coating can provide a minimum of two years' protection in the marine environment (as seen on some of the aluminum oxide panels). This is consistent with other research [15], which reported good salt water corrosion resistance for aluminum oxide plasma spray coatings.







After Marine Exposure

5086 Al with Al203

FIG. 12-Plasma spray coated panels before and after marine exposure.

Metallic/Ceramic Coatings

Results shown in Table 6 for exposure times up to 31 months indicate that coatings M and O are providing the best corrosion protection. Slight pinhole rusting was noted on a few of the coating M nuts (within 25 months' exposure) and on some of the coating O fasteners (within seven months). The extent of corrosion for coating O fasteners did not progress beyond pinhole rust through 31 months. The white corrosion products, present on both coatings, are typical for aluminum and zinc-based coatings exposed to marine conditions [8, 14].

Coatings P-R exhibited slightly reduced corrosion resistance compared to coatings M and O. Slight pinhole rusting was evident on coating P fasteners through 31 months and moderate pinhole rusting on coating Q and R fasteners through 31 and 30 months, respectively. Coating N was the least corrosion resistant of the coatings evaluated. Failure of this coating, denoted by base metal rust, occurred on all fasteners within the first nine months of exposure.

It is worth noting the variability in corrosion performance between coatings M and N. These coatings can both be classified as inorganic zinc, and they vary only in their potassium silicate binder ratio. The reduced corrosion resistance of coating N was not due to the coating composition, but was attributable to the method of coating application. These fasteners were coated in the manufacturer's laboratory in a preliminary setup to determine the feasibility of application by a dip/spin process. The poor marine performance of the coating strongly suggests inadequate coating coverage.

Conclusions

1. Thermally sprayed Zn-Al pseudo alloy coatings provided a minimum of 34 months' protection to steel substrates under severe marine atmospheric conditions. Thermally sprayed aluminum and zinc coatings provided a minimum of 42 months' protection in this environment. 2. Of the two ceramic coatings evaluated, the aluminum oxide (Al_2O_3) provided the best protection for aluminum substrates under marine atmospheric conditions.

3. The extent of corrosion observed on the sealed aluminum oxide-titanium dioxide ceramic coating was much less than that noted on the same coating in an unsealed condition.

4. Metallic/ceramic coatings M (zinc-base) and O (aluminum-base) provided a minimum of 31 months' protection to steel substrates under severe marine atmospheric conditions.

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Computer Techniques in Corrosion Protection

REFERENCE: Průšek, J., "Computer Techniques in Corrosion Protection," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 220-226.

ABSTRACT: The development of a problem oriented corrosion expert system (CES) is described. The CES has the following aims: (1) compilation of corrosion data files from data obtained by experimental activities or from analyses of practical results, (2) analysis of corrosion problems (determination of environmental aggressivity, degradation mechanisms, and corrosion kinetics) with the use of corrosion data bases and generalized theoretical knowledge, (3) optimizing the selection of technology for the protection of engineering plant, machines, and products from corrosion, and (4) economic analysis of the individual corrosion protections suggested.

Corrosion technologists and designers can utilize CIS to (1) file the results of corrosion research for subsequent application in corrosion analysis and evaluations and (2) objectivize, upgrade, and speed up the designing of corrosion protection including its economic evaluation.

The structure of the software has been devised for the interactive solution of problems. A dialogue of the user and the computer permits protection design optimizing.

KEY WORDS: optimization, design, computers, corrosion protection, corrosion forecast, data base

The present level of theoretical knowledge and experimental results in the field of corrosion and material protection have prepared conditions for a proposal of a problem oriented corrosion expert system (CES) [1.2].

One of the duties of designers is to assess the problems related to the effects of aggressive environments on the performance properties and durability of technical products. Demands on the performance properties of a particular plant, machine, or product, and an analysis of the corrosion effects provide a basis for the designing of suitable protective measures that would rule out or suppress all the possible negative influences of environment on the product.

The criterion of an optimized corrosion protection design is to ensure protection of maximum durability at the lowest possible cost of its application and maintenance during the entire life required.

To resolve responsibly the protection, the designer should know the character and measure of aggressivity likely to endanger the product, and has to assess the type and degree of possible corrosion damage. A design of optimum protection should be based on extensive expert knowledge as well as on availability of complete sets of corrosion, technological, and economic data applicable in technical practice. Corrosion protection designs have not always been fully effective. Failures of protective measures caused by incorrect designs are responsible for most of the existing corrosion losses.

The present trends towards savings in metals, raw materials, and energy make correct selection of corrosion protection a highly demanding task on all decision-making levels of manage-

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ment. The newly designed, problem oriented computerized corrosion expert system (CES) is a highly effective tool helping the corrosion experts and designers in their responsible work. Using a computer, it is now possible to analyze specific corrosion problems and design a corresponding protection. The decisions made by the computer are based on generalized knowledge in the field of the corrosion of metals and in that of corrosion protection.

Concept of the Corrosion Expert System

The basis of CES is a general model of the procedure used to select optimum corrosion protection (Fig. 1). By means of the input data, that is,

- (1) the type of product, its expected performance properties and the required life, and
- (2) the characteristics of the prevailing environment in which the product is to serve,

it is possible to determine, for selected types of materials and protective systems, all the required output data substantiating the design of an optimum protective system.

The structure of the system software is shown in Fig. 2. CES consists of packages of users and system programs. The software has been devised for resolving the most frequent corrosion problems. The CORA and EDATA programs are intended for corrosion scientists and technologists, while the application programs for the design of optimum corrosion protection systems, classified according to the respective environment to ATM, WATER, SOIL, TEMP, should serve as tools for designers. The support EDRA and EDATA software facilitates checking, scanning, and revision of programs as well as their supplementing, updating, and independent scanning of data bases.

The main programs contain sequences of interlinked subroutine files. They comprise gener-



FIG. 1-Basic model of the procedure used in selecting an optimum corrosion protection.



FIG. 2—Elementary structure of the CES software.

alized decision making procedures concerned with corrosion, corrosion technology, and economy. The software structure is based on system processing of particular conditions for corrosion, their analysis, and on algorithmized procedures producing the results of the solutions.

Internal cooperation with the data base files is a necessary prerequisite in computer analyses of corrosion problems. The data base files in fact constitute the supporting thesaurus of knowledge. Access to the data bases is ensured by the programs. Whereas the program software is generally applicable and valid, and data bases can be compiled so as to apply exclusively to a certain region or country (for example, sets of paint types are classified according to the manufacturing program in a certain country, or with respect to specific stipulations of national standards, and so forth). The software allows the user to cooperate simultaneously and optionally with a number of data bases of exclusive validity.

The individual creation of data bases and selective access to them permit the CES software to be generalized on an international level. The system is capable of respecting the national differences as well as providing conditions for comparisons between different variants of solutions. In this way it is possible to ensure substitution of protective materials or systems by others imported from, or available in, another country, including economic evaluation of the respective alternatives.

The designing of corrosion protection invariably involves some risks, so that it is necessary to ensure a certain probability that the solution has been correct. The computerized processing of an extensive data base creates suitable conditions for rendering the conclusions as objective as possible.

Interactive Operation of the System

The operation of the CES is started by calling the input program (Fig. 2). The user has a choice of a number of main programs for his particular problems and purposes. The main program chosen then controls automatically the sequence of computing, feeding in the input data, its analysis, evaluation, and processing of the final solution.

The computer works on the principle of interaction. The task is resolved in direct contact with the user, in fact in a dialogue between the operator and the computer. The software allows the computing procedure to be backspaced and the task conditions changed. It permits solution variants to be obtained when using alternative data bases.

Examples of the Main Software for the System

The structure of the main CORA program, devised for corrosion analysis, estimation of the course of corrosion, or the time during which a certain degradation is to be expected, is shown in the flow chart in Fig. 3; a part of subroutines MATM for atmospherical environments is shown in Fig. 4.

In the application of the system, use is made of the corrosion aggressivity classification ap-



FIG. 3-Flow chart of main program CORA.



FIG. 4—Flow chart of the subroutine MATM.

proved by Working Group 4, International Standards Organization (ISO) Corrosion of Metals and Alloys (TC 156) [3,4]. The classification is based on environmental data (time of wetting, sulfur dioxide $[SO_2]$, and Cl^- content) as well as on corrosion data (annual corrosion losses of steel, zinc, aluminum, and copper). The classification criteria stipulated in COMECON standards are also respected [5]. The system allows for the possibility of creating a degradation function and deriving conclusions from empirical approximative relationships suggested by a number of authors.

The structure of the main ATM program devised for optimized designing of systems protecting steel from atmospheric corrosion is shown in Figs. 5 and 6. The procedure for entering the input data is illustrated by the flow chart of subroutines DEM. Following analysis of the conditions for corrosion, possible protection methods are recommended and the consequences of unprotected weathering steel are specified. The technical, technological, and economic evaluation of the individual solution can then be chosen by the user.



FIG. 5-Flow chart of the main program ATM continued.

Hardware for the System

The already finished parts of the system have been operated with the use of the Hewett Packard (HP) 9835 computer. The software is written in BASIC. In view of the interactive character of operation the system should utilize a personal computer. The functionally verified part of the system uses a working store of 64 kB capacity, an external disk store, a CRT display, and a printer output.

The data base and program pack is stored in the external fixed store. According to the course of the dialogue, the selected program is automatically transcribed into the working store of the computer. The data bases providing the necessary data and information for decision making are called simultaneously. According to the conditions entered and the users requirements, the interactive work with the computer proceeds until the corrosion problem is gradually resolved.

Conclusion

The principal philosophy used in the creation of the CES is based on the interactive character of its operation. The computer is regarded as a partner in dialogue with the user who influences the computer function as well as the degree of its utilization, and has a priority in the resolving of the individual technological and economic problems of corrosion protection. The main con-



FIG. 6-Flow chart of the main program ATM.

tribution of the computer is its rapid and qualified formulation of decisions in relation to the users requirements, and its ready retrieval of the necessary information from the data bases.

The algorithmization of procedures for the design of protection from atmospheric corrosion has already been resolved. The software, in the form of the CORA, ATM, EDROU, and EDATA main programs, is ready for use. The structures of general data bases have been devised, for example, technological data bases for application in Czechoslovakia. The system is ready for the introduction of further data bases, and the validity of the outputs can be readily expanded to cover additional fields.

The problem oriented CES can be utilized separately as well as extended to include further applications. For instance, the system can be included in a program for automatic designing of steel structures for new investment projects, or in an information system dealing with environmental factors in industrial regions, and so forth. In such instances, CIS can either be operated separately, or its parts can be introduced as suitable subroutines into another system.

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Environment Characterizations

Environmental Effects in the Atmospheric Corrosion of Zinc

REFERENCE: Cramer, S., Carter, J. P., Linstrom, P. J., Flinn, D. R., **"Environmental Effects in the Atmospheric Corrosion of Zinc,"** *Degradation of Metals in the Atmosphere, ASTM STP 965,* S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 229-247.

ABSTRACT: The Bureau of Mines, U.S. Department of the Interior, as part of the National Acid Precipitation Assessment Program, is conducting a field exposure program to measure the corrosion damage on commonly used structural metals and the incremental effects of acidic deposition and other environmental variables. Corrosion damage, air quality, rain chemistry, and meteorology are being continuously measured at five sites in the Eastern and Midwest United States for periods up to 84 months. Corrosion damage on zinc for periods up to 36 months was determined from weight-loss measurements, analysis of corrosion film chemistry, and of precipitation runoff chemistry. The results suggest the long-term zinc corrosion film consists of a stable inner layer sensitive to atmospheric sulfur dioxide (SO₂) concentrations and a nonprotective outer layer. A synergistic reaction involving SO₂ and nitrogen dioxide (NO₂) may occur. Dry deposition of SO₂ and NO_x on the corrosion film is substantial. Zinc losses from the corrosion film are proportional to hydrogen ion loading. Covariance between many air quality and rain chemistry variables may be low enough to avoid, to a considerable degree, problems in developing linear regression models of corrosion damage.

KEY WORDS: corrosion, atmospheric corrosion, zinc, air quality, rain chemistry, meteorology, corrosion film chemistry, runoff chemistry, hydrogen ion load, sulfur dioxide, nitrogen oxides, acidic deposition, wet deposition, dry deposition

As part of the research of Task Group VII-Effects on Materials, within the National Acid Precipitation Assessment Program (NAPAP), the Bureau of Mines (BOM), U.S. Department of the Interior, is conducting a field exposure program to measure corrosion damage to commonly used structural metals. The purpose of this research is to determine the effects of acidic deposition and other important environmental variables on corrosion damage, and to establish a data base for testing various physicochemical models of corrosion damage from which dose/ response relationships or damage functions can be developed. Accurate assessment of environmental effects on corrosion damage requires concurrent measurements of air quality, rain chemistry, and local meteorology. Five sites where these measurements are continuously recorded have been established in the East, Northeast, and Midwest of the United States. Two of these sites have been operated since 1982. Metals being studied by the BOM at these sites are 1010 carbon steel, Cor-Ten A, 110 copper, 191 zinc (high-purity rolled zinc), 3003-H14 aluminum, and two coated-steel products, galvanized steel, and Galvalume. Other weathering studies are being conducted at these sites by the Environmental Protection Agency on industrial and household paints, and the National Park Service and Geological Survey on dimension stone. A

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description of the field exposure program, including onsite monitoring activities and aerometric and rain chemistry characteristics, has been reported [1]. Zinc corrosion data from this program are the focus of the present paper.

The atmospheric corrosion of zinc has been widely studied in laboratory and field exposures [2-7]. Much of a general nature is known about the zinc corrosion process. However, specific details of the chemical and physical processes, and complex interactions between these processes, which allow one to assess changing environmental conditions and determine their effect on corrosion, are not nearly as well known. In this paper, seasonal variations in air quality and rain chemistry at four of the exposure sites are described. Covariance between environmental variables that may affect linear regression models of atmospheric corrosion is examined. The effects of environmental factors on the dissolution of the corrosion film and their implications concerning corrosion film chemistry are discussed. Finally, evidence is presented from three-year exposures that the corrosion film consists of an outer layer that is relatively unprotective, and an inner layer sensitive to sulfur dioxide (SO₂) concentrations that controls the corrosion process in long-term exposures.

Experimental Program

Field exposure corrosion tests are conducted at five sites, which are located at Research Triangle Park, NC, Washington, DC, Chester, NJ, Newcomb, NY, and Steubenville, OH. Air quality, rain chemistry, meteorology, and particulate chemistry are monitored continuously at these sites. A combination of federal, state, local, and private organizations are conducting the environmental monitoring activities [1]. A smaller methods site for trials of new experiments is operated without environmental monitoring at the BOM Avondale Research Center. The test site on the roof of the West End Library in Washington, DC (Fig. 1) is typical of the five sites. Three types of exposure experiments, boldly exposed, sheltered, and runoff, are being conducted [1]. Only the boldly exposed and runoff experiments are discussed here.

Boldly Exposed Measurements

Zinc specimens are prepared and exposed using ASTM recommended procedures for atmospheric corrosion tests [1]. Exposed specimens are mounted on a rack facing south and inclined 30° with the horizon. Weight-loss panels measure 10 by 15 cm (4 by 6-in.) and are exposed in triplicate. Microanalysis coupons, intended for subsequent surface analyses, are exposed with the weight-loss panels and measure 2.5 by 4.5 cm (1 by 1.75-in.). Specimens are exposed for periods of 1, 3, 12, and 36 months; exposures up to 84 months are in progress. In addition, pairs of specimens with one side masked off are being exposed to measure skyward and groundward effects at the New York and Washington, DC, sites. Corrosion film weights and corrosion weight loss are measured gravimetrically. Corrosion film compositions are measured by wet chemical analysis of the weight-loss panel stripping solutions [1].

Runoff Measurements

Measurements to determine corrosion film losses in precipitation runoff are conducted only at the Washington, DC, site. The runoff experiment is similar to the boldly exposed experiment except that it involves a single large zinc panel, which is fitted with a special polyethylene tray to collect all of the precipitation draining from the skyward side of the panel. The runoff is funneled into a container for subsequent chemical analysis [8]. The runoff panel measures 0.2 m² (1 by 2 by ft) on one side. A Type 304 stainless steel panel is used as a control to determine runoff effects from a relatively inert surface for comparison with the zinc runoff results. Runoff samples from the zinc and stainless steel panels and a rain chemistry sample are collected monthly for analysis. The monthly runoff samples and the rain chemistry sample are analyzed



FIG. 1—Washington, DC, exposure site on roof of West End Library showing: test racks for metal. paint, and building stone; collectors for rain chemistry specimens; and sampling line for air quality measurements.

for hydrogen, sodium, potassium, calcium, magnesium, ammonia (NH_4) , chlorine, nitrate (NO_3) , sulfate (SO_4) , and zinc. A skyward side corrosion experiment is conducted concurrently with the runoff experiment to provide data on the weight loss and corrosion film composition of the zinc runoff panel. With these data, a mass balance on the runoff panel corrosion film yields directly the amount of dry deposition on the panel

$$D_i = R_i + A_i - W_i \tag{1}$$

where for the *i*th chemical species and measured per unit of runoff panel surface area

- W = wet deposition: the input to the panel surface from rain and snow; determined from the analysis of the rain chemistry sample,
- A = corrosion film accumulation: determined from the composition of corrosion film on the skyward side corrosion panel exposed for the same time as the runoff panel,
- R = runoff: the output from the panel surface; contains contributions from both wet and dry deposited material plus that leached from the corrosion film; determined from analysis of the runoff sample, and
- D = dry deposition: the input to the panel surface from dusts, aerosols, and adsorbed gaseous species.

Corrosion Product Characterization

Corrosion films from selected zinc microanalysis specimens have been examined by scanning electron microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, ion scattering spec-

troscopy, and thermogravimetric analysis (TGA); the results are reported elsewhere [9]. Additional TGA analyses were performed on zinc specimens exposed 1 to 36 months. One set of measurements was made in helium at atmospheric pressure. A second set was done under vacuum using a Veeco SPI-10 monopole residual gas analyzer (RGA) and an ionization pressure gage to measure the composition of gases produced during thermal decomposition of the corrosion film. Corrosion film weight-loss measurements were made using a Cahn RH electrobalance. A Cahn Mark II time derivative computer was used to generate weight-loss rate curves. Both weight-loss and weight-loss rate were recorded at a nominal heating rate of 5°C/min over the temperature range 40 to 250°C. For measurements under vacuum, the composition of the gas produced by thermal decomposition was determined at roughly 5-min intervals.

Results and Discussion

Environmental Variables

The air quality and rain chemistry data exhibited seasonal behavior that was typical for each of the variables. These observations were made by inspection of three years of monitoring data; they are meant only to indicate whether the data from the different sites are periodic.

Air Quality—Average gaseous pollutant concentrations computed for the 24-month period 1983 June to 1985 May are given in Table 1. Except for SO₂ at the Washington, DC, site, these values are similar to those reported earlier [1]. The Washington, DC, SO₂ value represents a 35% reduction from 1982 levels. High nitrogen oxide (NO) levels are characteristic of the DC site and should be considered in terms of possible synergistic corrosion effects involving SO₂ and NO₂ at low relative humidities [10, 11]. Figure 2 is a plot of monthly average SO₂ concentrations for the Washington, DC, and New York sites. The cycle of maximum SO₂ levels in the winter and minimum levels in the summer is in good agreement with historic patterns related to regional energy demands. With two exceptions, a similar pattern was observed for NO and nitrogen dioxide (NO₂) at each of the sites. Nitrogen oxides are too low at the New York site for any pattern to be observed. Nitrogen dioxide is high all year at the Washington, DC, site and exhibits no periodic behavior. Ozone has a cycle that is shifted by 6 months from those for SO₂, NO, and NO₂, and is characterized by a maximum concentration in the summer and a minimum concentration in the winter.

Rain Chemistry—Monthly ion loading, defined as the product of ion concentration and monthly rain volume divided by the cross-sectional area of the rain collector, is used here as a measure of the total exposure of a material to an ion species. Figure 3 is a plot of monthly hydrogen ion loads at the Washington, DC, and New York sites. The hydrogen ion load reaches a maximum during the summer and a minimum in the winter. This cycle is roughly 6 months out of phase with the cycle for SO₂ shown in Fig. 2. Other ions, such as SO₄, NO₃, and NH₄, follow the same cyclic pattern as the hydrogen ion load.

Table 2 lists correlation coefficients computed from monthly air quality and rain chemistry data obtained at each site over a two year period, 1983 July to 1985 June. The correlation between rain volume V and the hydrogen ion load H_L is perhaps of the most interest. One would

	-	•		
Site	SO ₂	NO	NO ₂	03
North Carolina	3.0	7.9	12.7	27.3
Washington, DC	10.2	38.4	33.5	17.5
New Jersey	8.3	5.3	15.5	31.8
New York	2.8	0.2	1.3	31.0

 TABLE 1—Average pollutant concentrations in ppb. 1983 June through 1985 May.



FIG. 2—Monthly average SO₂ concentrations at Washington, DC, and New York sites: data set, 1982 March through 1985 December.



FIG. 3—Monthly hydrogen ion load at Washington, DC, and New York sites; data set. 1982 June through 1985 June.

expect, since H_L includes rain volume in its computation, that the correlation would be strong. Instead the correlation coefficient ranges from 0.42 for the Washington, DC, site to 0.84 for the New Jersey site, that is, from a weak correlation to a moderately strong correlation. Similar values are observed for the interactions V-SO_{4L} and V-NO_{3L}. Table 2 shows high correlations between ions associated with acidic deposition, H_L -SO_{4L} and H-NO_{3L}, and with atmospheric aerosols, NH_{4L}-SO_{4L} and NH_{4L}-NO_{3L}. On the other hand, there is no correlation or relatively weak negative correlation for SO₂-SO_{4L}, NO_X-NO_{3L}, H_L-SO₂, and H_L-NO_X. The results in Table 2 suggest that covariance (or multicollinearity), while not to be discounted in developing

	Correlation Coefficients						
Interaction	NC	DC	NJ	NY			
V-H,	0.62	0,42	0.84	0.50			
V-SO ₄₁	0.65	0.54	0.79	0.44			
V-NO ₃	0.68	0.63	0.80	0.65			
H_1 -SO ₂	0.06	-0.34	-0.41	0.26			
H_{1} -NO,	-0.42	-0.58	-0.34	-0.26			
H ₁ -SO ₄₁	0.98	0.93	0.97	0.89			
$H_1 - NO_3$	0.94	0.85	0.92	0.73			
NH41-SO41	0.88	0.82	0.88	0.84			
NH41-NO1	0.94	0.88	0.84	0.77			
SO ₂ -SO ₄	-0.05	-0.41	-0.48	-0.40			
$NO_X - NO_{3L}$	-0.55	-0.60	-0.30	-0.20			

 TABLE 2—Correlations between air quality and rain chemistry variables.

 1983 July through 1985 June.

linear regression models for corrosion damage, may not be a significant problem for a number of important air quality and rain chemistry variables, including rain volume and hydrogen ion load, sulfur dioxide and sulfate ion load.

Zinc corrosion damage has been shown to vary directly with the atmospheric concentration of $SO_2[2,4.6,10,12-14]$. In one study, Schikorr [14] shows that the monthly average corrosion rate of zinc closely followed the annual cyclic variation in SO_2 concentration. The corrosion data from the present study were examined for seasonal trends. None were found in the data from the North Carolina, Washington, DC, and New Jersey sites for exposures of 1, 3, or 12 months. The absence of such trends suggests that other environmental factors, such as time of wetness (TOW), are important in the zinc corrosion process. (Temperature and humidity data are being assembled for each site but are not yet available.) On the other hand, data from the New York site exhibited cyclic behavior for all three exposure periods. Maximum corrosion rates in January through February. This does not coincide with the pattern identified by Schikorr [14] for SO_2 or identified here for any of the other air quality or rain chemistry variables. However, freezing temperatures during winter at the New York site will result in a low TOW, which one suspects is at least partially responsible for the low corrosion rates observed during the January through February period.

Corrosion Film Chemistry

In the absence of acidic deposition and marine influences, the atmospheric corrosion of zinc involves first the formation of zinc oxide, or hydroxide [9]. Equilibration with atmospheric carbon dioxide (CO₂) then leads to the formation of basic zinc carbonates [15]. The various reactions and equilibria involved in these processes lead to the reaction paths shown schematically in Fig. 4. Loss of zinc from the corrosion film can occur by two such paths. In clean environments, those free of acidic deposition, the zinc hydroxide (Zn(OH)₂) or zinc carbonate can dissolve in precipitation and wash from the surface in a manner described by $K_{sp,1}$ and $K_{sp,2}$. When acidic species are present in wet or dry deposition, a second path involving the reaction of hydrogen ion with the basic zinc corrosion product is available. A soluble salt, such as zinc sulfate (ZnSO₄), which can be washed from the metal surface, is the product of this second reaction. Two moles of H⁺ are needed to free a mole of Zn from Zn(OH)₂; only one mole of H⁺ is required for zinc carbonate (ZnCO₃) forming the soluble bicarbonate ion [9]. The rate of neutralization in this second reaction path will depend on the kind of acidic species delivered to the zinc



FIG. 4-Schematic representation of reactions and equilibria involved in forming zinc corrosion film.

surface, its rate of delivery in wet or dry deposition, its residence time on the surface, and the presence of other species that may influence the reaction.

Zinc corrosion film weights, which are roughly related to corrosion film thickness, are shown in Fig. 5. Each vertical bar represents data from 25 one-month exposure tests (involving three panels per test), fourteen 3-month exposure tests, and eleven 12-month exposure tests. The corresponding number of tests for the Ohio site are 12, 4, and 1. The vertical bar represents the range of the mean film weights (that is, the mean for the three panels in a test) observed in the tests. The horizontal line dividing the bars represents the average film weight for all of the tests. The horizontal line for the three-year exposures represents the one test completed at each of the sites (except for Ohio). The considerable dispersion in the film weights reflects the sensitivity of the corrosion film to environmental conditions. The minimum corrosion film weights at each site increased with exposure time. The average corrosion film weights also increased with time. This increase was rapid for the Washington, DC, site, particularly after three-months exposure, moderate for the New Jersey and New York sites, and slow for the North Carolina site. The substantial corrosion film present after only one month of exposure would suggest that the corrosion product forms rapidly and that the zinc surface is covered by corrosion product within hours or days of its initial exposure.

Zinc corrosion rates are shown in Fig. 6 for the same set of tests as presented in Fig. 5. The vertical bars represent the range of the mean corrosion rates (that is, the mean for the three panels in a test) observed in the tests. The solid black bar represents the standard deviation computed from replicate measurements and indicates the precision of the measurements. The midpoint of the solid bar locates the average corrosion rate for all tests. The wide dispersion in the corrosion rates for the shorter exposures indicates the importance of environmental conditions during the initial exposure. Such variations in corrosion rate are common in much of the field data reported for short exposures [1-5]. Figure 6 shows that most of these variations have damped out after one year. Except for the Washington, DC, site, mean monthly corrosion rates fall by a factor of 2 after 3-months exposure and by a factor of 2 again after 12-months exposure, indicating that the corrosion product offers some degree of protection to the underlying zinc. However, from one to three years there is little decrease in the corrosion rate at the New York, New Jersey, and North Carolina sites, and the corrosion rate actually increases by 50% at the Washington, DC, site. This, coupled with the substantial increase in film weight with time shown in Fig. 5 would suggest that continued film growth in long exposures makes little or no contribution to the overall protection of the zinc.



FIG. 5—Zinc corrosion film weights for five field sites and four exposure periods. Shaded bar represents the range of mean film weights observed in individual tests; horizontal line dividing the bar is average film weight for all tests: data set, 1982 March through 1985 December.

Zinc corrosion films produced in 1-month to 3-year exposure periods all gave similar TGA weight-loss curves. The features of these curves include a gradual but increasing weight loss with increasing temperature and then, for measurements in helium at atmospheric pressure, a rapid weight-loss from 200 to 250°C. For the TGA-RGA measurements in a vacuum, the rapid weight-loss began at temperatures 20 to 30°C lower (Fig. 7). (Temperature control was more difficult in the vacuum. This lead to fluctuations in the heating rate, which prevents direct comparison of the weight-loss and weight-loss rate curves in Fig. 7.) The TGA measurements were consistent with a film composed of basic zinc carbonate, $ZnCO_3 \cdot nZn(OH)_2$. The similarity of the TGA weight-loss curves for corrosion films produced in both short- and long-term exposures suggests that conversion of the initial $Zn(OH)_2$ into the basic zinc carbonate begins as soon as the initial corrosion product forms. Measurements on specimens exposed one month and three years at the Avondale, MD, site using the combined TGA-RGA technique showed that CO_2 and H_2O were produced by the thermal decomposition of the corrosion film (Fig. 7), indirect evidence that the zinc corrosion product contains both the carbonate and the hydroxide. The relative amounts of these two compounds as a function of temperature (and roughly of time) can be computed from the data in Fig. 7 by assuming that the partial pressures for CO_2 and H_2O are proportional to the molar production of these gases from the corrosion film. The integrated area under the curves, after establishing a reasonable baseline, is then proportional to the total molar production of the gases. Using these areas, the mole ratio H_2O/CO_2 is 1.5, which is the value that corresponds to the basic zinc carbonate film $2ZnCO_3 \cdot 3Zn(OH)_2$ [16].



FIG. 6—Zinc corrosion rates for five sites and four exposure periods. Shaded bar represents the range of mean corrosion rates observed in individual tests; solid bar represents standard deviation of replicate measurements; average corrosion rate for all tests is midpoint of solid bar; data set. 1982 March through 1985 December.

Corrosion film analyses by wet chemical techniques showed the amount of sulfur present in the films was low. Sulfate is not a major constituent of the corrosion films. After 1-month exposure at the Washington, DC, site, the measured accumulation of sulfur in the corrosion films averaged 8 mol % compared to the amount of zinc in the film. It tended to remain at this level in longer exposures, and the sulfur concentration after three years had increased only to 10.0 mol %.

The wet and dry deposition of sulfur, nitrogen (as NO₃), calcium, and sodium on zinc exposed one and three months at the Washington, DC, site is summarized in Table 3. The corresponding wet and dry deposition values for stainless steel are included for comparison. The deposition values were computed from runoff measurements using Eq 1. Calcium, a constituent of dusts and ash, not surprisingly is delivered to the panels primarily as dry deposition. Sodium, which is often explained as a constituent of sea salt but is also a significant constituent in ash [16], is delivered in roughly equal amounts in wet and dry deposition. The dry deposition of calcium and sodium on the zinc and stainless steel surfaces is similar and suggests that, at least in short exposures, both surfaces have roughly the same efficiency as collectors of the characteristic particulates containing these elements. On the other hand, the dry deposition of SO₂ is much higher on zinc than on stainless steel. To a lesser extent, this is also true of NO_x. If it assumed that the adsorption of NO_x and SO₂ on the stainless steel is small, that is, that all of the dry deposition on stainless steel is caused by nitrate and sulfate aerosols, and that a similar amount of nitrate and sulfate dry deposition occurs on zinc, then the increased dry deposition of



FIG. 7–TGA and RGA results for corrosion film on zinc microsample C-67 exposed three years at the Avondale. MD. methods site.

sulfur and nitrogen on zinc can be interpreted as a result of SO_2 and NO_x absorption by the zinc corrosion product. In the case of sulfur, the figures in Table 3 clearly indicate that the zinc corrosion film is a strong absorber of SO_2 . This fact is further accentuated by knowing that the deposition measurements reported here were made in the June-Aug period when atmospheric SO_2 concentrations were, lowest and wet deposition of sulfate was highest. Despite these conditions, the sulfur deposited by dry deposition was nearly as great as that by wet deposition. A similar analysis shows that NO_x is also absorbed by the corrosion film. However, the analysis also shows that NO and NO_2 , which generally have much higher atmospheric concentrations than SO_2 at the Washington, DC, site, are much less readily absorbed than SO_2 .

The results of the runoff measurements in terms of solution chemistry are shown in Fig. 8. The lines in this figure are a graphical presentation of the equilibria given in Fig. 4. The small cross-hatched area represents the range of pH and zinc concentrations observed in the runoff samples collected over a seven-month period, June-December 1985, at the Washington, DC, site. The bracket at the lower left corner of the figure shows the pH of the incident rain. The brackets above it show the range of Zn^{2+} concentrations that would result if all the H⁺ neutral-

		1 Month		3 Month			
		Dry			Dry		
Element/Metal	Wet, μ mol cm ²	μmol cm ²	% of Total	- Wet, μmol cm ²	μmol cm ²	% of Total	
S-Zn	0.37	0.34	48	0.89	0.99	53	
-SS	0.37	0.10	21	0.89	0.20	18	
N"-Zn	0.33	0.16	32	0.69	0.45	40	
-55	0.33	0.13	28	0.69	0.32	32	
Ca-Zn	0.059	0.334	85	0.234	1.045	82	
	0.059	0.401	87	0.234	1.214	84	
Na-Zn	0.024	0.033	58	0.065	0.064	50	
-ss	0.024	0.022	48	0.065	0.057	47	

 TABLE 3—Wet and dry deposition on zinc and stainless steel (SS) at Washington, DC, in a one- and three-month exposure in 1985.

"N as NO₃, does not include NH₄.



FIG. 8-Monthly zinc runoff results and related equilibria; data set. June through December 1985.

ized either $Zn(OH)_2$ or $ZnCO_3$. In addition to a curve describing the solubility of $ZnCO_3$, there are curves for amorphous $Zn(OH)_2$ and for α - $Zn(OH)_2$. Pourbaix [17] indicates that these forms of zinc hydroxide are more likely to exist under the neutral to slightly acid conditions that occur on the outer surface of the corrosion film than the less soluble ϵ - $Zn(OH)_2$. In any case, this figure shows that the solubility of the zinc corrosion product is orders of magnitude higher than the concentrations that exist in the runoff. Saturation of the runoff in zinc ions, even in a thin boundary layer adjacent to the film surface, would appear unlikely. The narrow range of near neutral pH values observed for the runoff, 6.58 to 6.74, indicates that the corrosion film has reacted with nearly all of the acidic species present in the precipitation.

Runoff data are reported in Table 4 for the June-December 1985 measurements; H_L is the

Month			R, mg Zn/dm ²		
	H_L , mg H/dm ²	V_L , L H ₂ O/dm ²	Observed	Fitted"	
June	0.0940	0,478	4.27	4.74	
July	0.0641	0.554	3.43	3.96	
August	0.0643	0.574	4.61	4.00	
September	0.0365	1.441	5.00	5.84	
October	0.0549	1.088	6.16	5.34	
November	0.0527	0,908	5.00	4.67	
December	0.0064	0.159	1.98	0.73	

TABLE 4—Zinc runoff data from Washington, DC, June through December 1985; $H_{L} = hydrogen ion load$, $V_{L} = rain volume load$, and R = zinc runoff lossfrom the corrosion film.

 ${}^{a}R = (\alpha_1 + \alpha_2 [\mathrm{H}^+]) V_L.$

monthly hydrogen ion load, V_L is the monthly rain load, and R is the zinc lost from the corrosion film in runoff. These data were fit by least squares to the two-parameter model

$$R = (\alpha_1 + \alpha_2 [\mathrm{H}^+]) V_L \tag{2}$$

where $H_L = [H^+]V_L$, and $[H^+]$ is the hydrogen ion concentration in the incident rain. This equation was reported in a slightly different form earlier [9]. α_1 represents the solubility of the corrosion product in neutral precipitation; α_2 represents the grams of zinc dissolved from the corrosion film per gram-equivalent weight of hydrogen ion consumed in neutralization reactions with the zinc corrosion product (Fig. 4). Both processes (solubility and neutralization) occur concurrently during field exposures; separating them in Eq 2 is done only to facilitate analysis of the data. With a correlation coefficient of 0.42 for the Washington, DC, site (Table 2), H_L and V_L can be treated as independent variables in computing α_1 and α_2 . The results of these calculations are shown in Table 5 (DC runoff) using H_L and V_L alone as explanatory variables and then together. T-scores indicate that the α 's are significant for each of these cases. However, the higher R^2 would suggest the combination of H_L and V_L is the preferred model for the runoff data. This result leads to a solubility of 3.2-mg zinc dissolved from the corrosion film per litre of precipitation. The α_2 value of 34.2 is close to the stoichiometric value of 32.7 for the dissolution of Zn(OH)₂. It suggests that Zn(OH)₂ is the principal constituent neutralized in the corrosion film at the Washington, DC, site in short-term exposures.

	V _L Co	V _L Coefficient		H_L Coefficient	
Independent Variable	α1	t-Score	α2	t-Score	R ₂
DC runoff (short term)					
H_L only	•		70.9	5.8	0.85
V ₁ only	5.09	7.5	• • •		0.90
H_{l} and V_{l}	3.18	4.8	34.2	3.6	0.97
Weight-loss experiments					
H_{I} only	· 		93.2	31.5	0.91
V ₁ only	4.21	25.5		0	0.86
H_L and V_L	0.10	0.2	91.0	6.6	0.91

TABLE 5-Effect of H_L and V_L on zinc runoff losses.^a

 ${}^{\boldsymbol{\alpha}}\boldsymbol{R}_{L} = (\alpha_{1} + \alpha_{2} [\mathrm{H}^{+}]) \boldsymbol{V}_{L}.$

Runoff results can also be calculated from the boldly exposed weight-loss data. Zinc lost from the weight-loss panels is equal to the total metal loss less the amount of zinc retained in the corrosion film. Runoff results calculate in this way for 3-, 12-, and 36-month exposures at the North Carolina, Washington, DC, New Jersey, and New York sites were fitted to Eq 2. The results (weight-loss experiments) are shown in Table 5 in the same format used for the runoff data. While H_L and V_L alone are both significant explanatory variables, only the H_L term is significant when they are combined. For this reason and the slightly higher R^2 , H_L was chosen as the explanatory variable. The runoff results based on the weight-loss data and the fitted curve are plotted in Fig. 9. The α_2 value of 93.2 is higher than the stoichiometric value of 65.4 associated with the dissolution of ZnCO₃. It suggests that other environmental species in addition to H_L contribute to film dissolution in the longer exposures. The high value of α_2 also indicates that per mole of hydrogen ion, the zinc corrosion film dissolves more rapidly in these exposures than in short-term exposures at the Washington, DC, site.

Weight-Loss Measurements

The loss of corrosion products in the runoff as a result of hydrogen ion and other acidic species, particularly the higher loss rates observed in long exposures, raises the question of whether the corrosion film is ever completely stripped from the panels. The results in Figs. 5 and 10 would indicate that this does not occur. Zinc weight loss is shown in Fig. 10 as a function of zinc runoff in one- and three-year exposures at four sites plus a three-year exposure at the



FIG. 9—Zinc runoff and hydrogen ion loading data from weight-loss experiments at the NC, DC, NJ, and NY sites in exposures of three months to three years; data set, 1982 March through 1985 December.



FIG. 10—Zinc weight loss and runoff data from five sites in exposures of one and three years; data set. 1982 March through 1985 December.

Avondale, MD, methods site. A mass balance on the corrosion film shows that the zinc weight loss from the panel M is given by

$$M = M_A + M_R \tag{3}$$

where

 $M = \text{zinc weight loss, mg/dm}^2$,

- $M_A = \text{zinc}$ accumulated in the corrosion film; determined from corrosion film analyses, mg/dm^2 , and
- M_R = zinc runoff; measured as the difference $(M M_A)$, mg/dm².

The derivative of Eq 3 with respect to M_R is

$$\frac{\partial M}{\partial M_R} = \frac{\partial M_A}{\partial M_R} + 1 \tag{4}$$

At steady state conditions, when there is no further growth in the corrosion film, $\partial M_A/\partial M_R$ should be zero and the zinc weight loss should equal the corrosion film runoff loss, that is, $\partial M/\partial M_R = 1$. However, as Fig. 10 shows, $\partial M/\partial M_R = 1.35$ and $\partial M_A/\partial M_R > 0$, indicating that even after one- and three-years exposure zinc is accumulating in the corrosion film. There are some site-to-site differences in the slopes computed from the data in Fig. 10. The Washington, DC, and New York sites have slopes of 1.65, while that for New Jersey is 1.20 and North Carolina is 1.16.

Zinc weight-loss data are plotted in Fig. 11 versus exposure time for 3 year exposures at each of the sites, and a series of 1 year exposures at the Washington, DC, and North Carolina sites. The shape of the short-term curves varies considerably. As noted earlier, this is typical for such data and related to the importance of environmental conditions during the initial exposure.



FIG. 11—Zinc weight loss curves for three-year exposures at the four sites and a series of one-year exposures at the Washington, DC, and North Carolina sites; data set, 1982 March through 1985 March.

Figure 11 that shows the instantaneous corrosion rates (slope of the curves) levels off with time or in the case of the Washington, DC, site, actually increases. This is not the result expected of protective corrosion films when the film thickness is continuing to grow (Fig. 5). Nor is it the behavior exhibited by the corrosion films in short exposures where an increase in film thickness produces a decrease in corrosion rate (Figs. 5 and 6). In long exposures the increase in film thickness beyond a certain value appears to offer no real improvement in corrosion protection. This would suggest that the long-term corrosion film may consist of two layers, a stable inner layer with considerable control over the corrosion process and a nonprotective outer layer that continues to grow. This outer layer would be affected to a greater extent by all of the weathering processes that affect the corrosion film: TOW, H_L , dry deposition, runoff, basic carbonate formation. In short exposures, while the two-layer structure is developing, these processes would affect both layers of the corrosion film; hence, the strong influence of environmental factors on corrosion rate observed in exposures up to a year. However, in long exposures where the twolayer structure is well developed the sensitivity of the corrosion kinetics to some of these factors is reduced.

The existence of a two-layer structure in longer exposures is also suggested by the ordering of the three-year weight-loss values (Fig. 11), an ordering that is totally different from that which would be inferred from the short-term data. For the first time the ordering of metal damage would appear related to atmospheric SO₂ concentration. Slopes of the weight-loss curves for long exposures were computed by the difference between the one- and three-year weight-loss values. The slopes are shown in Table 6 expressed as equivalent annual weight loss and as corrosion penetration (in μ m/year). Also listed in Table 6 are the hydrogen ion load for the final two years of the specimen exposure and the average SO₂ concentration for this period. Weight-loss values do not correlate well when plotted versus H_L ; the value for the Washington, DC, site is a distinct outlier from those for the other sites. On the other hand, there is a good, if nonlinear, correlation of weight-loss with average SO₂ concentration (Fig. 12).

The development of a stable inner layer sensitive to SO_2 concentration may lead to conditions where other environmental factors also become important. For example, Kucera [10] and Byrne and Miller [11] have both indicated that SO_2 and NO_2 can act synergistically under relatively dry conditions to produce sulfuric acid

$$SO_2 + NO_2 + H_2O \rightarrow H_2SO_4 + NO$$
(5)

Site	$H_L,$ mg/dm ²	Average SO2, ppb	Annual Weight Loss, mg/dm ²	Equivalent Corrosion Rate, μm/year
New York	0.861"	2.75"	51.5	0.72
North Carolina	0.694 ^b	3.00 ^b	46.3	0.65
New Jersey	1.399 ^b	8.13 ^b	75.9	1.06
Washington, DC	1.270"	10.17"	135.8	1.90

TABLE 6-Long-term zinc corrosion damage computed from 12 and 36 month exposure data.

"Measured 1983 June through 1985 May.

^bMeasured 1983 March through 1985 February.



Average SO2 Conc., ppb

FIG. 12-Effect of SO₂ concentration on long-term corrosion damage.
Kucera has cited evidence for this reaction on carbon steel and copper. Byrne and Miller, based on chemical analyses of corrosion film and condensate, indicate that it may also occur on aluminum. Haynie et al. [13] examined the possibility for such a reaction on galvanized steel and found none, but the SO_2 and NO_2 levels chosen may not have been suitable for establishing such an effect. Relative to the other sites, the environment at the Washington, DC, site would seem more likely to meet the conditions needed for Reaction 5 to occur. The Washington, DC, site has a relatively low annual time-of-wetness, and NO_2 concentrations are high. Furthermore, runoff measurements indicate that dry deposition of NO_x occurs on the corrosion film at this site. Thus, a two-layer corrosion film may be a reasonable concept to use in explaining the long-term corrosion behavior of zinc. The stable inner layer is sensitive to ambient levels of SO_2 . A mechanism, such as Reaction 5, then accounts for the much higher corrosion rate observed in long exposures at high NO_x sites, such as the Washington, DC, site.

Conclusions

Zinc exhibits different short-term and long-term corrosion performance related to environmental conditions and the nature of the corrosion film. Zinc corrosion in long exposures (exceeding one year) depends on atmospheric SO₂ concentration. A synergistic relationship between SO₂ and NO₂ may exist where conditions favor the oxidation of SO₂ to form sulfuric acid (H₂SO₄), that is, relatively dry conditions and significant dry deposition of NO₂. Zinc corrosion rates are level or increasing in long-term exposures even though the corrosion film continues to grow. A two-layer structure is suggested by the fact that film growth in long-term exposures does not improve the corrosion protection. In this model, a stable inner layer sensitive to SO₂ concentration controls the long-term corrosion kinetics of the zinc. The outer layer is relatively nonprotective, responsive to weathering processes, and continues to grow. In short exposures, before the two-layer structures is well developed, the zinc corrosion rate is strongly influenced by the effects of environmental conditions on both layers.

The zinc corrosion film begins transforming into a basic zinc carbonate as soon as corrosion product is formed. $2ZnCO_3 \cdot 3Zn(OH)_2$ was identified in the long-term corrosion product. Approximately 8 to 10 mol % sulfur relative to zinc is present in the corrosion product for all exposures. Significant amounts of SO₂ and to a lesser extent NO_x are deposited in the corrosion film by dry deposition. The loss of zinc in runoff from the corrosion film is directly proportional to H_L . In short exposures at the Washington, DC, site, the principal constituent dissolving from the corrosion film is $Zn(OH)_2$; in long exposures it appears to be $ZnCO_3$. The correlation coefficient for rain volume and H_L ranged from weak to relatively strong. In general, covariance was sufficiently low between many of the air quality and rain chemistry variables of interest that problems in developing linear regression models of corrosion damage may, to a considerable degree, be avoided.

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DISCUSSION

T. J. Summerson¹ (written discussion)—Are there any plans to extend the studies to western site locations?

You reported only on the rolled zinc sheet. What have been the results for carbon steel, aluminum, and these other materials?

S. Cramer, J. P. Carter, P. J. Linstrom, and D. R. Flinn (authors' closure)—A site near Carus, OR, was located by the Bureau of Mines to serve as a "clean" or reference site for indexing the environmental effects at the five earlier sites. The site, operated by the Oregon Department of Environmental Quality, had continuous monitoring of some air quality and meteorological parameters, and could have been expanded to the operating standards of the other sites. It had a temperate climate, adequate rainfall, and most importantly, excellent air quality and a rain pH 1 to 2 units higher than rain at the other sites. Unfortunately, the Environmental Protection Agency (EPA) and National Acid Precipitation Program (NAPAP) did not fund its operation.

On the other hand, California has an extensive materials effects program funded by the California Air Resources Board, which addresses some of the unique problems of the western states,

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that is, fogs, minimal precipitation, and high levels of the nitrogen oxides. Much of this work is focused on the environment of the Los Angeles basin.

Limited results for carbon steel, aluminum, and the other materials have already been published in several sources. Additional results will be forthcoming in National Association of Corrosion Engineers (NACE), ASTM, and other publications, particularly as data from the longterm exposures becomes available. NAPAP will use this data in preparing the 1989 assessment document and later the final report on materials effects scheduled for 1992.

Using the Classification of Corrosivity of Atmospheres to Extend the Service Life of Materials, Structures, and Products

REFERENCE: Vrobel, L. and Knotkova, D., "Using the Classification of Corrosivity of Atmospheres to Extend the Service Life of Materials, Structures, and Products," *The Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 248-263.

ABSTRACT: The resistance of products to atmospheric degradation is an important quality consideration. In Czechoslovakia, corrosion protection is considered to be an integral element of quality. The corrosion protection system is verified after each production step. The quality of the corrosion protection system is also confirmed by authorized state and departmental testing laboratories. Commissions of large industries concerned with atmospheric effects provide consultation and expert advice, especially in the application of international, national, and departmental standards and regulation.

The assurance of product corrosion resistance is an integral part of the quality control process. A system of coordinated standards covering general principles regulates construction, design, selection of materials, and protection systems. Emphasis is placed on the standardization of quality testing methods. Departmental and industry standards are now being developed. The physical and chemical principles of corrosion are incorporated in the approach used in these standards.

Every product is exposed to the atmosphere, either during manufacture or during its service life. The atmospheric environment varies from place to place and moment to moment. To select corrosion protection measures rationally for construction materials, it is necessary to know how the various atmospheric factors affect materials and the protective systems that are used with them. The generalization of this knowledge regarding the kinetics of the degradation of materials and protective systems, with information on the influence of the atmospheric factors, permits a practical classification system for atmospheric corrosivity to be developed. The essence of this classification system has been incorporated in national and international standards.

Active international cooperation among twelve member nations has allowed the International Standards Organization Technical Committee 156, Working Group 4 to produce four draft standards. This work summarizes many years of independent effort by the members.

The technique of classification of the corrosivity of the atmosphere is useful in making maps showing the corrosivity distribution for regions. It is also helpful in the detailed mapping of localities with variations in pollution levels. This approach is also used to select optimum corrosion protection measures and to develop testing procedures for products exposed to the atmosphere.

KEY WORDS: atmospheric corrosion, industrial pollution, marine pollution, time of wetness, classification criterion, corrosivity category

Construction materials and the products made from them become degraded by exposure to the atmosphere during transportation, storage, and operation. The relationship between the tendency for materials to become degraded by atmospheric exposure and the character of the atmosphere has been determined in a number of cases. However, interpretation of atmospheric degradation in terms of corrosion processes allows for more general use of the data.

¹Senior scientific workers, G. V. Akimov State Research Institute for the Protection of Materials, 250 97 Praha, Czechoslovakia. In Czechoslovakia, there is a system that translates information about protection against corrosion into practical designs required for technical applications. Corrosion resistance is considered an important aspect of the products and devices used in atmospheric environments, and measures designed to impart corrosion protection are integral quality features. These measures are checked at each stage of production. Authorized state testing shops have been set up to follow the quality of these protective measures. International, national, and local standards with the advice of qualified experts are used in designing appropriate protective measures.

Other countries, including the USSR and Sweden, also emphasize the atmospheric corrosion resistance of materials and products. Committees of experts concerned with these problems collaborate with national standardization authorities and institutes concerned with corrosion and determine appropriate techniques for securing corrosion resistance. This work is valuable not only in terms of optimizing the use of materials, but also in terms of improving the nation's economy. Only products with sufficient resistance to atmospheric corrosion can compete in international trade, especially in exports to Third World developing nations. The requirements of international trade also provide an impetus for developing a classification system for atmospheric corrosion. Standards and regulations relating to a variety of products could refer to such a classification system.

Standards on Atmospheric Corrosion Resistance

A coordinated system of standards has been developed in Czechoslovakia to guide designers and engineers in the selection of materials for service in corrosive environments. These standards emphasize the need to conduct tests and inspections to determine the severity of the applications. Various protective measures are evaluated by considering the function of the product and the degradation processes that may be encountered. Towards this end, it is necessary to evaluate or at least estimate the corrosivity of the environment in which each product is used. It is also possible to estimate the life of various protective systems used on products in corrosive environments. The lives of these alternative systems can then be evaluated in terms of the needs of the product involved. This analysis allows the selection of an optimum protective system by comparing the life of each protective system with the requirements of the product.

The selection process for a protective system is illustrated in Fig. 1. The Czechoslovakian standards which provide guidance for this process are listed in Table 1. At the conclusion of this process it is necessary for the product design and manufacturing engineers to incorporate these recommendations into specific product designs.

A set of standards has been developed in Czechoslovakia to provide guidance in selection measures to combat corrosion and other forms of environmental degradation. The approach used in this effort is illustrated in the diagram below in Fig. 2.

Classification of Corrosivity of Atmospheres

Every product is exposed to an environment during its useful life that may influence its operation. The external environment is, in principle, the earth's atmosphere containing all of the corrosive components present in the local environment. However, when a product is put into use, a different environment may be created because of heat transfer to or from the environment, contamination of exposed surfaces, abrasive effects from contact with solid particles, and many other causes.

It is necessary to consider the working environment as well as atmospheric effects when evaluating the long-term performance of products and protective systems. It is also necessary to consider the conditions that occur during production, shipment, storage, and start up. In some cases, serious damage has occurred during these nonoperational periods.

The atmosphere is a complicated environment with a number of variables that affect corro-



FIG. 1-Selection of corrosion protection measures for products in atmospheric service.

Standards	Title	Description
CSN 03 8206	division lines of the globe into climatic region for technical purposes	the surface of the earth is divided into macroclimatic zones according to the cli- matic elements affecting the technical products
CSN 03 8804	The specification of protection systems of technical products against environmental effects	the principles of specifi- cation of protective sys- tems and the verification of their quality are deter- mined
CSN 03 8101	basic demands made on the testing of the quality of metal protection systems against corrosion	the basic demands made on the quality testing of the corro- sion protection systems are determined. The tests are divided according to purpose of use
CSN 34 5620	climatic tests selection of electrotechnical equipment in adverse climatic conditions	the kinds and degrees of the test severities in relation to the kind of product are specified
CSN 03 8805	kinds of climatic versions of technical products	in relation to the macrocli- mate, the category of the location and type of atmosphere of the kinds the product are specified

TABLE 1-Czechoslovakian standards for the protection of products against external degradation.

Standards	Title	Description
CSN 03 8203	corrosivity classification of atmosphere	in relation to the macro- climate, the category of the location and degree of pollution by SO_2 and chlorides for five degrees of corrosivity are classified
CSN 03 8204	the determination of an atmosphere's corrosivity for metals and metal coatings	the processes for the quantification of the corrosivity are specified
CSN 03 8004	quality of coatings on metals; terminology	the terminology and quality features of important coatings of metals and the informa- tive features of the de- preciation are stated
CSN 03 8110	testing of atmospheric corrosion resistance in functional conditions and on atmospheric test stations	the principles of the testing of the resistance of con- struction materials, pro- tection system products, and functional parts are outlined
CSN 03 8211	measuring the atmospheric pollution by sulfur dioxide	the absorption methods using alkaline plates are sketched
CSN 03 8260	protection of steel structures against atmospheric corrosion; Specifications, quality control, and maintenance	the selection, workmanship quality inspection, and maintenance of protec- tion systems of building steel structures against atmospheric corrosion in relation to the corro- sivity classification are specified
CSN 03 8240	protection of steel structures by paints against atmospheric effects	the quality features of protected surfaces and paints in relation to the corrosivity are specified
CSN 03 8207	protection of metallic products against climatic effects during storage	the definition of the corro- sivity classification for storage conditions with more precision and specification of protection modes are developed

TABLE 1—Continued.

NOTE: Additional standards covering specific types of coatings and laboratory corrosion tests are not listed.

sion. There is no single expression that can be used to estimate the atmospheric degradation of materials. In general, it is necessary to establish limits for the amount of damage that can be tolerated. Then the degradation processes that operate in the environment must be understood. It is necessary to estimate the extent of damage that may occur because of these processes and this must be compared to the limits established. Generally, it is desirable to have specialists carry out such an analysis.



FIG. 2—Czechoslovakian system of standards to provide guidance in the selection of protective measures.

An important component of this evaluation process is the classification of atmospheric corrosivity with respect to various materials for construction and protective systems. Specific levels of atmospheric corrosivity have been established for materials in terms of the damage that occurs. In the case of coatings, these corrosivity categories may be used in setting minimum requirements for surface preparation, coating thickness, and quality testing.

The classification of atmospheric corrosion of metallic material is presented in this paper. The results of tests at atmospheric exposure sites and in laboratory settings, as well as observations from the field, show that the corrosion rate of engineering metals is proportional both to the level of pollutants and the fraction of time that the metal surface is wet with moisture. Also the rate of corrosion decreases when stable and protective corrosion product layers form on metal surfaces. After a sufficient period of exposure, the corrosion rate achieves a constant value, which is a function of the fractional time of wetness and the level of pollutants in the atmosphere. However, the initial corrosion rates are more sensitive to the pollution level and fractional time of wetness than the long-term rates and so are more desireable in characterizing atmospheric corrosivity.

The results of past atmospheric corrosion studies are used in the preparation of Czechoslovakian standards CSN 03 8203 and CSN 03 8204 (Table 1). The corrosivity of the atmosphere is classified in these standards, and techniques for estimating the extent of corrosion damage are provided. Corrosion rates that may be used to design engineering metals over a range of atmospheric corrosivities have been identified as "guiding values." These Czechoslovakian standards were used as the basis for the work of the International Standards Organization Technical Committee 156 on the Corrosion of Metals and Alloys, Working Group 4, concerned with the Classification of Corrosivity of Atmosphere (ISO/TC156/WG4).

The classification of atmospheric corrosivity is in fact a generalization of our knowledge of the atmospheric corrosion of materials and coatings. As such it provides an essential link in the process of optimization of protective measures to combat corrosion [1]. The system diagramed in Fig. 3 is a specific version of Fig. 1 as applied to metallic materials.

This approach to the selection of materials should be followed for all types of products. However, it is necessary to obtain more precise information on the characteristics of atmospheric



FIG. 3—Diagram of the approach to selecting materials and protective systems for products containing metallic materials in atmospheric service.

exposures that influence corrosion rates, especially in terms of regional variations. Both the variation in the corrosion rate with atmospheric corrosivity and regional variations of atmospheric corrosivity have been monitored continuously in Czechoslovakia for the past ten years.

Special attention has been paid to the accumulation and processing of atmospheric data for the various macroclimatic zones, especially in Czechoslovakia. Measurements have been made of environmental characteristics, including pollution levels in important regions and areas of industrial activity. Maps have been prepared showing the distribution of corrosivity for the entire nation and detailed maps have been made for industrial regions and residential areas—for example, the city of Prague. Some of the results of this work are presented in Tables 2 and 3.

Long term studies on the corrosivity of some specific microclimates have also been carried out. These studies cover specific types of structures, such as bridges, and also include the effects of sheltering and occluded areas. Some examples of the results of this work are shown in Table 4 and 5. In spite of the difficulties of generalizing these results, they do provide important information on areas where the expected corrosion rates will be significantly different from those predicted from standard guiding values.

The results of statistically designed corrosion tests at various exposure sites are also included in the evaluation of atmospheric corrosivity and the development of the classification system. A very extensive set of results, including approximately 900 experimental values for steel, has recently been completed. These results were incorporated with the results of eight other test programs on sixty types of structural steels for a ten-year exposure period. A model developed from these results is not able to predict damage from corrosion in the atmosphere, but it is

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							Months						
Climatic zone	-	II	E	IV	>	I	VII	VIII	IX	×	XI	XII	Year
Moderately warm with moderate winter	166.2	211.6	230.2	258.4	306.4	312.5	328.2	340.0	381.4	135.0	•	•	
Moderately warm with cold summer	74.1	112.1	162.7	266.7	324.9	336.5	345.5	351.8	381.6	403.9	347.7	152.5	3259.9
CSSR in total	148.3	191.7	216.7	260.1	310.2	317.3	331.7	347.2	381.4	426.8	416.1	249.8	3599.3

TABLE 3—Number of hours with relative humidity of air equal to or higher than 95% and 80%.

								Months						
Climatic zone	Н, %	-	ш	III	2	>	٨I	VII	VIII	IX	х	XI	IIХ	Year
Moderately warm with moderate winter	95 80	128.1 560.1	104.2 459.4	73.9 372.7	48.5 285.1	54.3 308.6	54.7 512.5	61.0 328.2	67.6 346.1	96.7 382.4	148.0 465.7	155.1 542.6	178.5 606.2	1170.6 4970.6
Moderately warm with cold summer	95 80	162.7 573.7	138.8 481.9	125.1 445.6	96.6 547.0	86.3 334.1	78.0 337.1	71.3 343.5	87.3 351.8	105.5 385.8	166.6 459.7	254.2 564.0	252.1 616.4	1614.4 5242.4
CSSR in total	95 80	135.0 563.5	111.1 465.9	84.2 387.3	58.1 297.5	60.7 313.8	59.4 317.4	63.1 331.7	71.6 347.2	98.5 383.1	151.7 464.5	174.9 546.9	191.2 608.2	1259.4 5025.0

		Steel, g/m ²		Stee	el, %
of Location	Position of Specimens	11 523"	15 217 ^b	11 523ª	15 217*
Outside the bridge	vertically north	645	500	100	77.5
Category 1	vertically south	381	233	100	61.2
Under bridge floor	vertically	386	297	100	76.9
Category 2	horizontally from above	268	203	100	75.7
<u> </u>	horizontally from below	370	296	100	80.0

TABLE 4—Mass losses of steels after four-year exposure on steel bridge in urban atmosphere.

"11 523 = standard structural steel.

h15 217 = Atmofix weathering steel.

TABLE 5—Characterizing the microclimates of various categories of location in the same locality.

Characterization	Outdoors	Shelter	Storage
Duration of relative humidity 80% (% of time)	11.3	20.4	8.3
Indicated time of wetness OAY ^a (% of time)	42.9	58.6	0.1
SO_2 pollution ^b /mg/m ² /day	36.2	21.9	9.7
Rate of corrosion on carbon steel $g/m^2/day$	0.350	0.177	0.006

"Indication system of SVUOM with conductivity pickup.

^bMeasured on alkaline absorption plates.

useful for the analysis of the influence of individual variables [2]. This analysis did highlight limitations of the classification approach.

Joint test programs of SVUOM (G.V. Akimov State Research Institute) in Prague and SCI (Swedish Corrosion Institute) in Stockholm were important in this work. Similar exposures were carried out at eleven atmospheric exposure test sites in Czechoslovakia and Sweden. The atmospheric conditions covered by the sites in these two countries cover conditions typical of a very large area, including central and northern Europe, the United States, and Canada. This is a very important area in terms of the use of products. The results of the 4-year exposure have been published, [3.4] and the eight-year samples will be withdrawn starting in 1986. As a result of this work, we anticipate that we will be able to predict long term corrosion behaviour.

International Standardization of the Classification of Atmospheric Corrosivity

The ISO Technical Committee 156 on Corrosion of Metals of Alloys/Working Group 4 (ISO/TC156/WG4) is responsible for the classification of the corrosivity of atmospheres. This working group includes specialists from twelve countries bringing together many years of experience in atmospheric corrosion. This working group produced four proposals for standards concerning the classification of atmospheric corrosivity. These were registered by the Central Secretariat of the ISO in 1985. The titles of these documents are listed in Table 6.

The approach that has been used in ISO/TC156/WG4 for the classification of atmospheric corrosivity involves a consideration of the following significant factors that influence atmospheric corrosion:

- (a) time of wetness, including moisture condensation and precipitation,
- (b) pollution of the atmosphere by sulfur dioxide (SO_2) , and
- (c) the deposition of chlorides from marine sources.

ISO/DP 9223	corrosion of metals and alloys—Classification of corrosivity categories of atmospheres
ISO/DP 9224	corrosion of metals and alloys—Guiding values for the corrosivity categories of atmo- spheres
ISO/DP 9225	corrosion of metals and alloys—Aggressivity of atmospheres—Methods of measurement of pollution data
ISO/DP 9226	corrosion of metals and alloys—Corrosivity of atmosphere—Methods of determination of corrosion rate of standard specimens for the evaluation of corrosivity

TABLE 6—ISO draft proposals concerning atmospheric corrosivity classification.

These factors were chosen because of the strong effect that they have on atmospheric corrosion in most environments. Levels are proposed for each of these factors and used to develop an estimate of atmospheric corrosivity. Corrosivity is also classified into five categories for each of the four different metals. The mass loss corrosion damage after one year of exposure is the basis for determining the corrosivity category. These mass loss values are used only to determine corrosivity category and have no technical importance by themselves. They are, however, a necessary intermediate stage in the determination of corrosivity category. The guiding values of corrosion loss may be used to determine corrosion allowances in calculating the thickness of a supporting structural member or in determining the appropriate coating thickness.

It is important to note that the proposals cited in Table 6 provide a detailed methodology for determining corrosivity classification. The various classification tables from these proposals for time of wetness, sulfur dioxide, and chloride and the guiding values for corrosion plain carbon steel, zinc, copper, and aluminum are given in the Appendix (Tables A1 to A6).

Applications of the System for the Classification of Atmospheric Corrosivity

The estimation of the corrosivity of the atmosphere is the key input information for the selection of suitable corrosion protection measures as shown previously in Fig. 1. However, to improve the use of this approach in certain cases, we propose developing more detailed methods to estimate corrosivity categories based on the design and functional characteristics of the product or device in question. For example, this approach has been used for steel structures and motor vehicles in Czechoslovakia. Because of the complexity of the design in these cases, it has been necessary to carry out testing on model systems.

The use of the classification system of the corrosivity of the atmosphere has been codified in some legislation. Decree No. 105 concerning the documentation of construction requires that data used in developing the system of corrosion protection be taken from that published in the Codes of Law in Czechoslovakia. These data can be derived from the documents covering the classification of corrosivity in individual localities. Regional maps showing the distribution of corrosivities have become popular. However it must be noted that local effects created by the operation of the exposed technical product or adjacent operations can overwhelm the regional corrosivity effects.

Detailed mapping of the corrosivity appears to be suitable for large production plants that show significant variations in corrosivity. These maps can be used to select corrosion protection systems as well as to determine the time schedule for maintenance painting and recoating. In this case, it is necessary to use actual corrosion tests with standard specimens to develop the maps.

To determine the changes in the atmosphere as a result of new industrial activity, a network of measuring points is used with a central monitoring laboratory. The primary elements of this system or the partially processed data values may also be used for corrosivity estimation. The Municipal Information System (MIS) of the city of Prague supplies sufficient information to calculate the corrosivity of the atmosphere in the "living environment" circuit. The selection of corrosion protection measures can be optimized with this information.

Changes in the living environment in an area may cause economic damage, e.g., damage from corrosion [5]. These changes should be evaluated. The use of the guiding values of corrosion from the previously mentioned standards provides a rational method of evaluating corrosion damage. An example of this process is given in Table 7 for steel structures, and Table 8 provides an evaluation of service lives of various alternative protective coatings for steel based on their atmospheric corrosivity category and guiding value of corrosion. The use of this table precludes the necessity of integrating the complex corrosion kinetics involved in these corrosive conditions.

The draft proposals of the ISO/TC156/WG4 for atmosphere corrosivity classification have been recommended by the Working Group on Effects of the Influence of Pollution of the ECE UN as a suitable technical document for evaluating the effects of the environment on various objects and products. It was also recommended for the selection and optimization of protective measures as well as the numerical expression of damage. The classification of corrosivity thus provides an important contribution to the goals of the Convention on Long Range Trans-boundary Air Pollution.

Corrosivity Category (maximum steady state corrosion rate of carbon steel)	Version of Steel Structure					
Type of Structure	Standard Structural Steel with Paints	Atmofix Weathering Steel	Standard Steel, Aluminum 250 μm			
$3 \text{ to } 20 \ \mu\text{m}, \ \text{yr}^{-1}$						
light structures	1063	859	1263			
medium structures	1632	1835	1847			
4 to 40 μ m, yr ⁻¹						
light structures	1450	859	1263			
5 to 7 μ m, yr ⁻¹						
light structures	1954	unsuitable	1263			
medium structures	2171	1835	1848			

TABLE 7—Comparison of annual costs of the production and maintenance of	
steel structures at their 30-year service life, Kcs year ^{-1} .	

TABLE 8—Guiding service lives of coating systems of steel structures, years.

	Degree of Corrosivity of Atmosphere				
Kind of Corrosion Protection	1	2	3	4	5
$120 \ \mu m$ coat on manually derusted surface	20	10	5	< 5	< 5
120 μ m coat on blasted surface	30	20	10	5	<5
hot galvanizing, 60 to 80 μ m	50	50	40	20	10
hot spray of aluminum, 150 to 200 μ m	> 50	>50	>50	50	30
Electric metallization by aluminum, 60 to 80 μ m, coat	>50	> 50	>50	50	30

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Conclusion

The system of classification of the corrosivity of the atmosphere is a generalization of our knowledge of the atmospheric corrosion of materials. As such, it provides an important technique to optimize the selection of corrosion protection measures.

This system can be used to generate data bases that provide data on the corrosion behavior of materials and protective systems. The system may also be used in the evaluation of economic damage resulting from atmospheric corrosion.

To expand the proposed classification system, it is necessary to study in detail the corrosion that occurs in mildly aggressive environments, and especially to study the effect of combined pollutants, including the fall-out of ionizable materials. In view of the existing data, it is desirable to further subdivide Classes 1 to 3, thereby providing more precision in the method. It is also necessary to develop better knowledge of the atmospheric corrosion that occurs in extreme conditions, such as in tropical and arctic regions.

APPENDIX

Selected Tables from ISO/DP's or Atmospheric Corrosivity Classification

Unification of Time of Wetness According to ISO/DP 9223

	Time of W	'et ness	
Category	Hours/Year	% of Year	- Example of Occurrence
	<10	< 0.1	Internal air without climatic control
$ au_2$	10 to 250	0 to 1.3	Internal air without climatic control except for internal nonair-conditioned space in wet regions
$ au_3$	250 to 2500	3 to 30	Outdoor atmospheres in dry and very cold regions and properly ventilated sheds in temperate zones
$ au_4$	2500 to 5500	30 to 60	Outdoor atmospheres in all zones except for the dry trop- ical and extremely cold zones
$ au_5$	>5500	>60	Very damp regions, unventilated sheds in humid condi- tions

TABLE A1-Classification of time of wetness of corroding metallic surface.^{a,b,c,d}

"The time of wetness of a given locality depends on the temperature-humidity complex of the open air atmosphere and the category of the location.

^bThe column indicating the occurrence does not include all possibilities following from the degree of sheltering.

^cIn indoor atmospheres without climate control wetted by operational sources of vapor, times of wetness of τ_3 to τ_5 can be attained.

^dFor times of wetness τ_1 and τ_2 , the corrosion proceeds according to probability laws (probability and frequency of critical values affecting environmental factors). The probability of corrosion is higher for surfaces on which dust may settle.

Classification of Pollution Categories According to ISO/DP 9223

Pollution categories are defined for pollution of the atmosphere by SO_2 and for airborne salinity. These two kinds of pollution are representative of atmospheres such as rural, urban, industrial, and maritime.

Deposition Rate of SO ₂ , $mg/m^2/d$	Concentration of SO ₂ , $\mu g/m^{-3}$	Category
< 10	<12	Po
>10 to 35	>12 to 40	\mathbf{P}_1
>35 to 80	>40 to 90	\mathbf{P}_2
>80 to 200	>90 to 250	\mathbf{P}_3

TABLE A2—Classification of pollution by sulfur-containing substances represented by SO2.^{a,b,c,d,e,f}

"Methods of determination of SO₂ are specified in ISO/DP 9225.

^bThe SO₂ values determined by the deposition (Sd) and volumetric (Sc) methods are equivalent for the purposes of classification. The relationship between measurements using both methods could be approximately formulated as Sd = 0.8 Sc.

 $^{\circ}$ For the purposes of this standard, the SO₂ deposition rate and concentration are expressed as the annual average. The result of short-term measurements may differ considerably from long-term averages. Such results serve for guidance only.

^dAny concentration of SO₂ up to P₀ is considered to be the background concentration and is insignificant from the point of view of corrosive attack.

^rPollution by SO₂ over P₃ is considered extreme and is typical of operational microclimates beyond the scope of this standard.

In shed atmospheres and especially in indoor atmospheres, the concentration of the pollutants is reduced depending upon the degree of sheltering.

Deposition Rate of Chloride $mg/m^2/d$	Category
3	S_
3 to 60	S ₁
60 to 300	S ₂
300 to 900	S _J

 TABLE A3—Classification of pollution by airborne salinity represented by chloride.^{a,b}

"The classification of airborne salinity according to this standard is based on the wet candle method specified in ISO/DP 9225.

^bDetermination of corrosivity categories are made from corrosion measurements on standard specimens according to ISO/DP 9223 and ISO/DP 9226.

NOTE: The classification of pollution by chloride (see Table A3) relates to outdoor atmospheres which are polluted by airborne salinity in marine environments.

 TABLE A4—Corrosion rates for the first year of exposure for the different corrosivity categories.^a

A	Cor	rosion Rates of M	letals, g/m²/year μ	m/year
Category	Steel	Zinc	Copper	Aluminum ^b
1	1 to 10 0.1 to 1.3	<0.7 <0.1	<0.9 <0.1	negligible
2	10 to 200	0.7 to 5	0.9 to 5	<0.6
	1.3 to 25	0.1 to 0.7	0.1 to 0.6	<0.25
3	200 to 400	5 to 15	5 to 12	0.6 to 2
	25 to 51	0.7 to 2.0	0.6 to 1.3	0.25 to 0.8
4	400 to 650	15 to 30	12 to 25	2 to 5
	51 to 83	2.0 to 4.2	1.3 to 2.8	0.8 to 2
5	>650	> 30	>25	>5
	>83	> 4.2	>2.8	>2

^aThe classification criterion is based on flat plate or helix specimens (see ISO/DP 9226).

^bAluminum experiences localized corrosion, but the corrosion rates shown in the Table are calculated as uniform corrosion.

NOTE: Numerical values for the first year corrosion rate for four standard metals are given in Table A4 for each of the corrosivity categories. The values cannot be extrapolated for prediction of long term corrosion behavior.

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Parameter	S ₀ -S	S_2	S ₃	S ₀ -S ₁	S ₂	S3	S ₀ -S ₁	S ₂	s,	S ₀ -S ₁	S ₂	S3	S ₀ -S ₁	S ₂	S ₃
1						JNALLOY	ED CARB	ON STEE							
P ₀ to P ₁	1	1	1 to 2	1	2	3 to 4	2 to 3	3 to 4	4	ę	4	S	4	ŝ	S
\mathbf{P}_2	-	I	1 to 2	1 to 2	3 to 4	3 to 4	3 to 4	3 to 4	4 to 5	4	4	ŝ	S	S	ŝ
P3	1 to 2	1 to 2	2	2	3	4	4	4 to 5	S	S	S	S	S	S	S
						Zinc	and Co	PPER							
P ₀ to P ₁	1	1	-		1 to 2	З	e	ы	3 to 4	ę	4	S	4	S	S
P ₂	T	1	1 to 2	1 to 2	2	e	e	3 to 4	4	3 to 4	4	S	S	S	S
P,	1	1 to 2	2	2	e	3 to 4	e	3 to 4	4	4 to 5	S	S	S	S	S
						A	TUMINU	5							
P ₀ to P ₁	1	2	2	1	2 to 3	4	ę	3 to 4	4	ę	3 to 4	S	4 to 5	S	S
P2	1	2	2 to 3	1 to 2	3 to 4	4	e	4	4 to 5	3 to 4	4	ŝ	4 to 5	S	S
Р,	1	2 to 3	e	2 to 4	4	4	3 to 4	4 to 5	5	4 to 5	5	S	S	S	5

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	4	lverage Corrosic (μm/year) fo	on Rate for the r the Following Categories:	First Ten Years Corrosivity			Steady State C or the Following	Orrosion Rate (g Corrosivity Ca	μm/y) tegories:	
Metal	14	26	3č	44	5	1 "	2 ^b	3¢	4q	5
Plain Carbon Steel Zinc	<0.5<0.1	0.5 to 2 0.1 to 1	2 to 10 0.5 to 2	10 to 35 2 to 4	>35 >4	~0.1 <0.01	0.1 to 1.5 0.01 to 0.5	1.5 to 6 0.5 to 2	6 to 20 2 to 3.5	> 20 3.5 to 8
Copper ^e Aluminum [/]	<0.01 ~0.01	0.01 to 0.1 <0.025	0.1 to 2 0.025 to 0.2	2 to 3 0.25 to 1.0	>3 >1.0	<0.01 0.01 to 0.02	0.01 to 0.1	0.1 to 1.5 0.02 to 0.2	1.5 to 3 0.2 to 1	ñ _ ^ ^
^a Applies also to the Ci ^b Applies to aluminum	u-Zn, Cu-Sn an of nurity 99 85	id similar alloys	with Cu conten	t of at least 60	%.					

Appres to autimutum of purity 93.65% min and autimum alloys which form solid solutions without admixtures of heavy metals.

"Structural plain carbon steel (Fe 360, ISO 630, St 3).

"In environments with corrosivity categories 1 and 2, interference colors are evident (oxides, sulfides). Ammonia accelerates corrosion; danger of corrosion cracking in case of copper alloys. /In environments with corrosivity categories 4 and 5, localized corrosion may occur if dust is present. Depth of penetration is up to 0.2 mm.

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Corrosion of Steel and Zinc in Scandinavia with Respect to the Classification of the Corrosivity of Atmospheres

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ABSTRACT: Exposure of steel and zinc specimens at 32 test sites in Scandinavia shows that the pollution by sulfur dioxide (SO_2) and by chlorides in marine locations is of decisive importance in the corrosion attack. The differences in the corrosion rate at the six rural sites in Southern Scandinavia are very slight despite substantial variations in other environmental parameters. Dose response relations for the corrosion attack on steel and zinc, including SO₂ concentration, chloride deposition rate, and time of exposure have been developed. The results may serve as a basis for a quantitative description of corrosivity classes in systems for classification of the corrosivity of atmospheres of the type which is now under development by the International Standardization Organization.

KEY WORDS: atmospheric corrosion, carbon steel, zinc, SO₂ pollution, chlorides, dose response relations, classification of corrosivity

Atmospheric corrosion is a process of great practical and economic importance that has attracted materials scientists for several decades. Extensive laboratory and field investigations have gradually improved knowledge about the qualitative, and in the last decades, the quantitative influence of climatic parameters on the atmospheric corrosion rate of the most important materials. Knowledge of the corrosivity of the atmosphere could be used for reduction of the corrosion damage by a rational choice of materials and protective measures. In some countries, standards or codes of practice have been issued including a classification system of the corrosivity of atmospheres [1]. This is also the case in Scandinavia, where the corrosivity classes, however, are mostly defined only in a qualitative manner [2,3]. During the last few years, a quantitative system for the classification of the corrosivity of atmospheres has been worked out that is within the scope of the International Standardization Organization (ISO)^{4.5}.

To improve knowledge in this field, a common Nordic exposure program coordinated

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⁴ISO DP 9223 Corrosion of Metals and Alloys-Classification of corrosivity categories of atmospheres.

⁵ISO DP 9224 Corrosion of Metals and Alloys—Guiding values for the corrosivity categories of atmospheres.

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through the Scandinavian Council for Applied Research, NORDFORSK, was started in 1975 at test sites with different types of atmospheres. The aim of the project was to map the corrosivity of the atmosphere in Scandinavia by exposure of carbon steel and zinc as reference materials and to find relations between corrosion and environmental parameters. The results from one and two years' exposure [4] and from four years' exposure [5] have been published previously. The present publication constitutes a final report after eight years' exposure. It contains all results obtained and an analysis of the influence of the most important climatic parameters on the corrosion attack. The results are then discussed in light of the above mentioned ISO classification system of the corrosivity of atmospheres.

Experimental Procedure

Test Sites

The exposure was performed at 32 test sites in Scandinavia (two in Denmark, five in Finland, six in Sweden, and the remainder in Norway). The locations of the sites are shown in Fig. 1. All sites, with the only exception the subarctic station in Gällivare, are located in Southern Scandinavia within the temperate climatic zone. Some of the sites are located in inland atmospheres that are either rural or have SO_2 as the main pollutant. Others are typical marine locations, while several are influenced both by manmade pollutants and airborne salinity, which is typical in Scandinavia because of the long coast line.



FIG. 1-Corrosion test sites in Scandinavia identified by the numbers found in Table 1.

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Measurement of Environmental Parameters

At most of the test sites, environmental parameters were measured. However for some of the sites meteorological data were used from the closest available meteorological site. The main environmental parameters of the sites are given in Table 1. This table also contains the corrosion attack on carbon steel and zinc after one year's exposure, which according to the above-mentioned ISO standard⁴, constitutes another way to characterize the corrosivity of an atmosphere.

The SO₂ content in the air in Sweden, Norway, and Denmark was measured by a volumetric method in which a known volume of air was passed through an absorption solution containing hydrogen peroxide. Air particles were retained in a filter prior to the solution. In Finland however, vertical alkaline impregnated filter papers were used to measure the SO₂ deposition rate, which has been converted to SO₂ concentration [4]. The different procedure used in Finland constitutes a source of uncertainty.

At most sites precipitation was also collected and analysed for certain constituents such as sulphates and chlorides, and for the pH-value. The chloride content in precipitation was used to assess the chloride deposition rate. Unfortunately, the wet candle method⁶ was not used for chloride determination. This makes a direct comparison of the corrosivity in marine locations with the ISO standard difficult.

The basic meteorological parameters—temperature and relative humidity—were measured continuously with thermohygrographs. These data have been used for calculating the mean temperature and the time of wetness. To estimate the time of wetness, the time at which RH > 80% at $T > 0^{\circ}C$ has been used.

Corrosion Measurements

The materials tested were carbon steel and zinc with the following composition:

Steel: 0.14 C, 0.42 Mn, 0.10 Si, 0.06 Cr, 0.017 P, 0.015 S, 0.01 Ni, 0.00 Cu

Zinc: 0.05 Fe, <0.0001 Cd, <0.001 Ti, <0.0005 Ni, 0.0007 Cu, 0.002 Pb, <0.0005 Al

For the carbon steel the extremely low copper content should be mentioned, which makes this steel more sensitive to corrosion attack than steels used in most other investigations. The zinc used was of electrolytic grade and very pure.

Test panels (100 by 150 by 1 mm) were exposed on racks at 45° to the horizontal (at 30° in Finland), facing south. The exposure started in July 1975, except in Denmark, where it started in July 1977. The zinc specimens were withdrawn after one, two and four years' exposure. The exposure periods for steel were one, two, four and eight years, with the exception of some Norwegian sites, where the last withdrawal was performed after 8.5 to nine years.

The corrosion attack has been established by evaluation of the mass loss. The corrosion products were removed by pickling. For the one and two years' exposure, the metal loss during pickling was corrected for through simultaneous pickling and weight-loss measurements of clean dummy specimens. For the four and eight years' exposure, pickling in at least four consecutive periods was adopted using the method of linear regression and extrapolation to zero pickling time for calculation of the weight loss. For pickling of steel, Clarks' solution was used. The zinc specimens were pickled in a solution of saturated ammonium acetate at room temperature.

Analysis of Results

Experimental data comprising the corrosion attacks and environmental data were subjected to statistical treatment and to regression analysis. The statistical model used is described in more detail below.

Results

Environmental Parameters

The main environmental parameters of the test sites are given in Table 1. The values are given as yearly averages.

Corrosion Attack for Steel and Zinc

The corrosion attack after one to eight years' exposure expressed as a reduction in thickness in micrometers are given in Table 2.

Corrosion Attack as Function of Time and Pollution

The corrosion attack on carbon steel and zinc as a function of time is illustrated in Fig. 2 and 3. A detailed analysis of the problem is given below.

Statistical Analysis and Development of a Statistical Model

Basic Principles

Since the quality of the environmental data from the different test sites varies and as some of the sites have special influencing factors, the set of test sites were subdivided into three groups before the statistical analysis.

The first group, denoted "A" in Table 1, consists of the sites that fulfill the following requirements:

1. Data on corrosion attacks on carbon steel are available from one, two, four and eight years' exposure.

- 2. The environmental data are measured close to or at the test location.
- 3. SO₂ concentration is measured continuously during at least one year.
- 4. No special pollutantlike cement dust strongly influences the environment.
- 5. Marine extreme conditions like the splash zone are excluded.
- 6. The test site must be located in the temperate climatic zone.

The second group, denoted "B" in Table 1, consists of test sites for which not all of the first three requirements are fulfilled.

Group "C" in Table 1 consists of the three test sites for which one of requirements 4, 5, or 6 is not fulfilled.

Group A was considered a suitable basis for regression analysis in terms of environmental factors and time of exposure. The mathematical model of corrosion attack thus obtained can then be used also for calculations on data from Groups B and C. The comparison in observed and calculated data may then be discussed.

		6 0							
					Meteorologic	al Parameters		Corrosion one Year's	rate after s Exposure
	Air	Precipitation	ı, mg/m² ∙ <i>d</i>		: : : :		Time of	-	i
Country, Site, Number	ыс. ив/т ³	SO4	σ	Hq	Frecipitation, mm/y	l emperature, C°	wetness, h/y	Steel, µm∕y	Zinc, µm/y
Sweden									
1 (C) Gällivare ^a	S	2.6	0.3	4.54	825	1.3	1577	ų	0.8
2 (A) Ryda	S	5.1	0.7	4.31	553	5.3	3440	17	0.7
3 (A) Stockholm Vanadis	32	7.6	1.6	4.46	470	6.3	2890	36	0.9
4 (A) Bohus Malmön 3	S	8.3	88	4.22	513	7.5	3258	67	1.9
5 (A) Bohus Malmön 1	ŝ	8.3	16.0	4.22	513	7.5	3258	34	1.1
6 (A) Gothenburg	16	15.0	12.3	4.27	700	7.2	3679	35	1.3
Finland								I	
7 (B) Salmisaari	20	6	ę	5.4	550	4.8	3171	39	1.1
8 (B) Harmaja	10	9	15	6.0	450	4.7	4091	36	1.2
9 (B) Otaniemi	15	7	2	4.7	540	4.6	3171	30	1.8
10 (B) Koski	e	4	2	4.8	580	4.7	3250	18	0.7
11 (B) Harjavalta	15	7	1	4.6	500	4.2	3127	31	1.1
Norway									
12 (A) Borregaard	85	26.4	5.8	3.73	615	6.2	2750	81	3.7
13 (A) Alvim	30	14.8	4.6	4.22	646	6.2	2750	35	1.4
14 (C) Brevik ^b	ŝ	36.4	10.3	7.54	825	5.8	2902	15	0.4

TABLE 1–Yearly averages of main environmental parameters and corrosion rates of carbon steel and zinc.

15 (B) Porserunn	×	17	ŝ	4.6	620	6.3	•	20	0.7
16 (A) Birkenes	• 4	14.5	5.0	4.18	1332	4.0	3483	17	0.8
17 (A) Tuentangen	æ	6.5	1.2	4.23	607	4.3	3071	18	0.6
18 (A) Folehavnen, 250 m	7	14.2	28.7	4.19	608	6.5	3071	49	1.6
19 (C) Folehavnen, 10 m ^c	9	42	639	6.0	480	6.3	3071	86	2.1
20 (B) Minde, Bergen	22	21	22	4.26	2174	7.5	3999	41	1.6
21 (B) Bergens Tidende	40	25	47	:	2600	6.2	:	49	1.8
22 (A) Hyllestad, Sogn	e	14.0	31.0	4.70	3214	6.6	3999	24	1.8
23 (B) Voss	:		:	:	1630	5.1		23	1.6
24 (B) Veritas, Bergen	28	25	47	4.6	2600	6.2	:	42	1.2
25 (A) Mongstad	ę	14.0	17.0	4.60	1303	7.2	3999	35	0.7
26 (A) Stend, Bergen	- 20	20	58	4.50	1781	6.6	3999	28	2.6
27 (B) Stord, I, 50 m	4	5	10	4.80	1293	7.5	3999	25	1.3
28 (B) Stord, II, 5 m	4	11	17	4.5	1150	7.5	3999	28	1.1
29 (B) Fredriksberg	22	21	22	4.26	2174	7.5	3999	34	2.3
30 (A) Tyholt	œ	2.0	10.0	4.80	1223	4.8	:	23	0.8
Denmark									
31 (B) Søborg	27	9	11	4.79	069	:	:	63	1.8
32 (B) Amager	11	S	4	4.62	551	•	•••	56	1.8
"Subarctic									
"Polluted by cement industry									
' Marine splash zone									

NOTE: A denotes sites with well defined environmental data, B denotes sites with incomplete data or some uncertainty on data quality, C denotes sites with extreme conditions.

						Cor	ROSION	Аттаск,	шĦ					
		St	eel							Zin	nc			
	one	year	two	years	four	years	eight	years	one	year	two y	ears	four	/ears
Country, Site, Number	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc	obs	calc
Sweden											3			
1 (C) Gällivare	9	18	×	27	17	41	30	61	0.8	0.6	0.9	1.3	1.4	2.6
2 (A) Ryda	17	18	26	27	42	41	56	62	0.7	0.7	1.5	1.3	2.1	2.6
3 (A) Stockholm Vanadis	36	3 6	56	59	86	89	108	134	0.9	1.3	2.1	2.6	4.2	5.1
4 (A) Bohus Malmön 3	67	55	81	83	66	124	177	187	1.9	1.6	2.4	3.2	5.0	6.5
5 (A) Bohus Malmön 1	34	25	44	37	67	56	104	84	1.1	0.8	2.0	1.6	4.5	3.3
6 (A) Gothenburg	35	31	54	47	60	71	125	107	1.3	1.0	3.1	2.1	5.9	4.1
Finland														
7 (B) Salmisaari	39 3	31	63	46	100	69	116	105	1.1	1.0	2.5	2.0	4.5	4.1
8 (B) Harmaja	36	28	77	42	122	63	202	95	1.2	0.9	2.5	1.9	4.5	3.7
9 (B) Otaniemi	30	26	53	40	87	99	89	60	1.8	0.9	3.4	1.8	5.9	3.6
10 (B) Koski	18	17	34	26	50	6 £	63	58	0.7	0.6	1.7	1.2	2.6	2.5
11 (B) Harjavalta	31	26	54	39	88	59	108	89	1.1	0.9	2.5	1.8	4.1	3.5

TABLE 2-Observed and calculated corrosion attack on carbon steel and zinc at one to eight years' exposure at test sites in Scandinavia.

								1	e I	·	(
82	137	123	229	186	341	279	3.7	2.5	7.0	5.1	15.0	10.2
39	S	59	89	88	107	133	1.4	1.3	2.3	2.5	4.8	5.1
22	20	33	26	50	37	76	0.4	0.8	0.4	1.5	0.9	3.0
22	34	34	53	50	:	76	0.7	0.8	1.4	1.5	2.3	3.1
19	28	29	48	43	69	65	0.8	0.7	1.6	1.4	2.6	2.7
21	28	31	45	47	64	70	0.6	0.7	1.3	1.5	2.2	2.9
31	61	47	66	71	137	107	1.6	1.0	2.8	2.0	6.4	4.0
287	134	432	159	650	204	979	2.1	7.7	3.2	15.4	7.6	30.8
40	S	60	85	16	133	142	1.6	1.3	2.8	2.6	5.7	5.1
65	66	67	100	146	166	220	1.8	2.0	3.8	3.9	7.8	7.9
29	3	44	51	99	83	107	1.8	0.9	2.9	1.9	4.8	3.8
:	82	:	46	:	:	:	1.6	:	2.4	:	3.4	:
55	82	83	86	125	:	189	1.2	1.7	2.6	3.4	5.4	6.8
23 4	0	35	6 6	53	130	91	0.7	0.8	1.3	1.6	2.8	3.1
45	2	67	56	101	68	157	2.0	1.4	2.6	2.7	4.1	5.4
21	2	33	56	49	88	78	1.3	0.7	2.5	1.4	3.2	2.9
24	39	36	55	55	:	83	1.1	0.8	2.4	1.6	3.8	3.2
40	46	60	75	16	127	142	2.3	1.3	3.8	2.6	7.6	5.1
24	33	37	48	55	76	83	0.8	0.8	1.4	1.6	2.5	3.3
39	86	59	151	89	197	137	1.8	1.3	3.7	2.5	7.6	5.1
24	8	36	137	55	193	84	1.8	0.8	3.4	1.7	8.1	3.3



FIG. 2—Corrosion attack on steel at some test sites in Scandinavia after one, two, four, and eight years' exposure.

Type of Models

Since Group A consists of 14 test sites, there are $4 \times 14 = 56$ independent data on corrosion attack on steel after one, two, four, and eight years' exposure. There are analogously $3 \times 14 = 42$ independent data on corrosion attack on zinc after one, two, and four years.

For carbon steel it is well known that the corrosion attack is a nonlinear function of exposure time during prolonged exposure periods of, for example, eight years [6, 7]. A fair description of the time course for a specific test site can usually be obtained by using the function.

$$K = at^n \tag{1}$$

where K is corrosion attack, t is time of exposure, and a and n are constants that may depend on environmental factors. The constant n usually is between 0.5 and 0.6. This type of model was chosen for carbon steel.

The corrosion attack on zinc is usually a linear function of time [8]. If the exposure conditions during the initial exposure period are extremely wet, a higher corrosion rate than that corresponding to the pollution level can be expected during the first one to two years. After this initial period, the corrosion rate decreases and attains "expected" values. This deviation from linearity can, however, not easily be described in terms of the average values of environmental factors. Hence the linear model

$$K = ct \tag{2}$$

where t is time of exposure and c is a constant, was chosen for zinc.



FIG. 3—Corrosion attack on zinc at some test sites in Scandinavia after one, two, and four years' exposure.

Regression Analysis of Steel Data

The mathematical model was constructed in three steps. First, the constants a and n were calculated for each test site from the time-course of the corrosion attack during the eight years. Linear regression analysis was then performed on constants a and n using the environmental factors of the different test sites in Table 1 as potential regressors. In combination with SO₂ concentration, only chloride deposition rate was significant as a regressor for a in Eq 1. The equation obtained was:

$$a = 0.75 \text{ SO}_2 + 0.51 \text{ Cl} + 16; \quad R = 0.96$$
 (3)

where

 $SO_2 = SO_2$ concentration, $\mu g/m^3$, and Cl = deposition rate of chloride, $mg/m^2 \cdot d$.

The exponent n in Eq 1 varies rather little between most test sites. As the regression equation obtained explained only 38% of the variation using the environmental data, the value of the exponent n was chosen as the average of n in Group A, i.e., 0.58. From these results the model for steel corrosion was formulated as:

$$K = (c_1 SO_2 + c_2 Cl + c_3) \cdot t^{c_4}$$
(4)

Finally, all the data of the well-defined test sites were used for a least-squares fitting to the model given in Eq 4. A general least-squares program with Taylor expansion as the method for linearization was used. Weighting of the data was performed with the assumption of a constant relative error. The following equation for the corrosion attack on carbon steel was obtained:

$$K = (0.77 \,\text{SO}_2 + 0.42 \,\text{Cl} + 14)t^{0.59}$$
(5)

where

K =corrosion attack on steel, μ m,

 $SO_2 = SO_2$ concentration, $\mu g/m^3$,

 $Cl = deposition rate of chloride, mg/m^2 \cdot d$, and

t = time of exposure, years.

The standard deviations for the constants denoted c_1 , c_2 , c_3 , and c_4 in Eq 4 were 0.08, 0.05, 1, and 0.03, respectively.

The model derived was tested by comparing observed corrosion attacks and corrosion attacks calculated from Eq 5 (see Table 2 and Fig. 4). The correlation coefficient for the data from one, two, four, and eight years' exposure of the test sites in Group A was 0.943, calculated as:

$$R = \sqrt{1 - \frac{\Sigma (K_{obs} - K_{calc})^2}{\Sigma (K_{obs} - \bar{K})^2}}$$
(6)

where \bar{K} = the arithmetic mean of the corrosion attacks of Group A.

The agreement between observed and calculated data for the well-defined sites of Group A may thus be considered good. If the analysis is also extended to sites from Category B, the spread around the line tends to be greater (Fig. 5). The outliers below the line from sites of Category B belong to the Finnish and Danish sites. A possible explanation is that the SO_2 depo-



FIG. 4—Comparison of calculated and observed corrosion attack on carbon steel at one, two, four, and eight years' exposure comprising all well-defined test sites (denoted A).



FIG. 5—Comparison of calculated and observed corrosion attack on carbon steel at four years' exposure comprising all test sites (A + B): \bigcirc sites of category A, \bigcirc sites of category B.

sition rate measurement underestimates the SO_2 concentration at the sites in Finland. At one of the Danish sites, an air-out-blow near the rack and at another, close proximity to a street treated with deicing salts may cause the high observed values.

Regression Analysis of Zinc Data

Multiple linear regression analysis of corrosion attack on zinc in terms of the environmental data in Table 1 confirmed that the time course is essentially linear. A least squares fitting of all data of the well defined test sites was performed in the same way as for steel using the following model:

$$K = (d_1 SO_2 + d_2 CI + d_3)t$$
(7)

The following equation for the corrosion attack on zinc was obtained:

$$K = (0.023 \operatorname{SO}_2 + 0.011 \operatorname{Cl} + 0.53)t \tag{8}$$

where

 $K = \text{corrosion attack on zinc, } \mu \text{m}$ SO₂ = SO₂ concentration, $\mu g/\text{m}^3$ Cl = deposition rate of chloride, mg/m² · d t = time of exposure, years

The standard deviations for the constants denoted d_1 , d_2 , and d_3 in Eq 7 were 0.004, 0.002, and 0.06, respectively.

The correlation coefficient defined according to Eq 6 for observed and calculated corrosion attacks of one, two, and four years' exposure of the test sites in Group A was 0.89. The observed and calculated data according to Eq 8 are given in Table 2 and for four-year values at test sites of Category A + B in Fig. 6.



FIG. 6—Comparison of calculated and observed corrosion attack on zinc at four years' exposure comprising all test sites (A + B): \bigcirc sites of category A, \blacksquare sites of category B.

Discussion

In classifying the corrosivity of the atmosphere, the corrosivity classes are usually defined using either the environmental parameters time of wetness and contents of sulphur pollutants and airborne chlorides or using the corrosion attack on standard specimens after one-year's exposure. In the present investigation, all sites have in principle been divided into three main types of atmosphere—rural, urban, and marine with a subdivision based on the pollution levels of SO₂ and chlorides. In Table 3, the sites are classified according to this system and values of corrosion attack for steel and zinc are given as illustrations. Using this table as a starting point, the influence of the main environmental parameters will be discussed.

Effect of Meteorological Parameters

The time of wetness defined as the time when the relative humidity exceeds 80% at temperatures above 0°C varies at the sites in southern Scandinavia between 2,750 and 4,100 hours per year. Also the total amount of precipitation shows big differences from around 500 to over 3,000 mm per year. A comparison of the results at rural sites with SO₂ levels <10 μ g/m³ shows that the corrosion rate of steel based on one year's exposure at six sites varies only between 17 and 23 μ m/year. Based on four years' exposure the difference in corrosion rate is even smaller—namely 11 to 13 μ m/year. This shows that the variations in the meteorological parameters have a minor effect on the corrosion rate within the limits occurring at the test sites of Southern Scandinavia. It also confirms that even in extensive areas within the temperate climatic zone, the pollution level is of decisive importance to the corrosivity of the atmosphere.

In the northern part of Scandinavia, in the subarctic zone represented by the test site Gällivare, the corrosion rate of steel in an unpolluted atmosphere is only six μ m/year. This may be ascribed to the long period with temperatures below 0°C. The time of wetness, 1,580 hours/ year, is thus substantially shorter than in Southern Scandinavia. Exposure of zinc in principle

				0	bserved Corr.	Rate, μm/yea	L. L.	Calculated	Corr. Rate	
Atmosphere, begination $mg/m^3 d$ \mug/m^3 one year four years steel zinc Site Rural R <5 <10 17 to 23 11 to 13 0.7 to 1.6 0.6 to 0.9 8 ryda, Koski, Porsgrunn, Bitkenes, Tuentangen, Voss Urban <5 <10 17 to 23 11 to 13 0.7 to 1.6 0.6 to 0.9 8 ryda, Koski, Porsgrunn, Bitkenes, Tuentangen, Voss Urban <5 <10 to 40 30 to 39 22 to 25 0.9 to 1.9 10 to 1.6 Stockhoin, Salmisarri, Arian Urban/marine <5 <10 to 40 34 to 53 1.3 to 24 1.4 to 2.0 6 to 15 0.9 to 1.6 Grebrog, Minde, Bergens Urban/marine <5 to 47 10 to 40 34 to 53 1.3 to 24 1.4 to 2.0 6 to 15 0.9 to 1.6 0.6 to 0.8 Mine, Min	Type of	CI ⁻ ,	n Level . SO ₂ ,	ste	el	zi	36		s Exposure, year	
	Atmosphere, Designation	mg/m²d	μg/m ³	one year	four years	one year	four years	steel	zinc	Site
	Rural R	\$	< 10	17 to 23	11 to 13	0.7 to 1.6	0.6 to 0.9	4 to 5	0.6 to 0.8	Ryda, Koski, Porsgrunn, Birkenes, Tuentangen, Voss
	Urban U1	N S	10 to 40	30 to 39	22 to 25	0.9 to 1.9	1.0 to 1.5	6 to 9	1.0 to 1.6	Stockholm, Salmisarri, Otaniemi, Harjavalta, Alvim
Urban 0 81 57 3.7 3.8 18 3.5 Borregard U2 02 < 24 to 36	Urban/marine U1/M1-2	5 to 47	10 to 40	34 to 63	19 to 38	1.3 to 2.4	1.4 to 2.0	6 to 15	0.9 to 1.9	Göteborg, Minde, Bergens, Tidende, Veritas, Fredriksberg, Søborg, Amager
Marine 5 to 20 <10 24 to 36 13 to 20 0.7 to 1.1 6 to 7 0.8 to 0.9 BM 1, Stord I, Stord II, MI 5 to 20 <10	Urban U2	9	>40 to 90	81	57	3.7	3.8	18	3.5	Borregaard
M2 20 to 100 <10 36 to 68 20 to 35 1.3 to 2.0 1.1 to 1.6 7 to 14 1.0 to 1.5 BM 3, Harmaja, Foliehavnen, 250 m M3 >100 <10	Marine M1	5 to 20	< 10	24 to 36	13 to 20	0.7 to 2.0	0.7 to 1.1	6 to 7	0.8 to 0.9	BM 1, Stord I, Stord II, Mongstad," Hyllestad,"
M3 >100 <10 86 40 2.1 1.9 Folehavnen, 10 m Subarctic A <5	M2	20 to 100	< 10	36 to 68	20 to 35	1.3 to 2.0	1.1 to 1.6	7 to 14	1.0 to 1.5	Stend BM 3, Harmaja, Folehonnen, 250 m
A <5 <10 6 4 0.8 0.4 Gällivare	M3	> 100	< 10	86	40	2.1	1.9	•	:	Folehavnen, 10 m
	Subarctic	<5	< 10	9	4	0.8	0.4	:	•	Gällivare

via based on the pollution level, and observed and calculated corrosion rates of carbon lim Š ç -5.5

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gives similar results showing corrosion rates in rural regions of 0.6 to 0.9 μ m/year. The exceptions are some sites on the Norwegian west coast, e.g., Voss, Hyllestad, and Stend. They show rather high corrosion attack (1.7 to 2.0 μ m/year) during the first year of exposure. This may be explained by the large amount of precipitation, which seems to have affected the corrosion rate of zinc at the beginning of the exposure period, as shown by Ellis [12]. This so-called memory effect may exert its influence during the first one to two years of exposure. After four years, the corrosion rate has decreased and at long-term exposure it seems to reach a value similar to that at the other rural sites (see Fig. 3).

Effect of SO₂ Pollution

The sulphur compounds, and especially SO₂, constitute the most important manmade pollutant in atmospheric corrosion today. The test sites may be divided into four categories according to the ISO Draft Proposal [4]: rural sites with $< 10 \ \mu g/m^3$ SO₂ and three urban categories: U1 with 10 to 40 $\mu g/m^3$, U2 with 40 to 90 $\mu g/m^3$, and U3 with 90 to 200 $\mu g/m^3$. To the U2 category belongs the Borregaard site, which has the highest corrosivity of all sites based on the four years' results for zinc and steel. The U3 class is not represented at all in the present network of test sites. A future study should also involve highly polluted sites. This would permit an assessment of the validity of the derived dose response functions for the whole interval of pollutant levels for which the classification system is intended.

In general, the corrosion rate of both steel and zinc at the SO_2 polluted sites is two to five times higher than at the rural sites. In the previous interim report, after four years' exposure, the corrosion rate at sites not strongly polluted by airborne chlorides correlated strongly with the SO_2 concentration. The following regression lines were reported:

$$K_4$$
 steel = 18.5 SO₂ + 292.5; $R = 0.88$, $V = 22\%$ (9)

and

$$K_4 \operatorname{zinc} = 1.1 \operatorname{SO}_2 + 14.6; \quad R = 0.88, \quad V = 22\%$$
 (10)

where

 K_4 = corrosion attack at four years' exposure given in g/m², SO₂ = SO₂ concentration in μ g/m³, R = correlation coefficient, and V = unexplained variance.

In Scandinavia, with its long coast, several important areas with combined SO_2 and chloride pollution can be found. In the U1 category, there are eight sites where sulphur pollution is accompanied by chlorides. The present model, which includes both a SO_2 and a chloride term, is thus an important development, which may be of substantial practical importance. However, it should be stressed that the functions given in Eqs 3 and 6 may be further developed and modified. For this purpose, the chloride deposition rate should be determined with the wet candle method rather than by using the value from the analysis of rain water. The reason for this is that the wet candle method seems to better reflect the influence of chlorides on corroding metal surfaces.

The corrosion attack on the sites with combined pollution are higher for both steel and zinc than they are in the U1 category without chloride pollution. The SO_2 content of the atmosphere seems to be of decisive importance for the corrosivity, however.

Effect of Chlorides

The marine sites have been divided into three categories M1 to M3. The pollution levels in the order of 5 to 20, 20 to 100, and >100 mg/m² · d chloride are based on values of combined wet and dry deposition rates in open precipitation gauges. The use of the chloride deposition rate instead of the distance from the shore is preferable, because the deposition strongly depends on local topography, prevailing wind direction, presence of archipelagos of islands, etc.

The results in Table 3 show that the corrosion rate for both steel and zinc increases with increasing chloride deposition rate. The test site with frequent sea water splash, Folehavnen 10, is the most corrosive in this category. Equations 5 and 8 are not valid for this site. If sites with extremely high chloride deposition rates should also be included, a nonlinear model with respect to chloride deposition might be useful. The analysis of the corrosion attack made after 1 and 4 years' exposure published previously may serve as an indication in this direction [5].

Effect of Other Parameters

Because of missing data from certain sites and in several cases because of small variations in a parameter within the region of Scandinavia as well as a certain lack of quality in climatic data, it is difficult to evaluate the influence of other variables. Such influences are expressed by the unexplained variance, which of course also contains the possible errors in data.

For steel, an analysis of the term $a \ge q 3$ shows that using the SO₂ and chloride levels, most of the variance in the experimental material may be explained. For the zinc corrosion attack given in $\ge q 8$, the unexplained variance is greater. The results show, however, that most of the corrosion attack in the investigated climatic zone may be explained by the two pollution parameters used.

In light of the ongoing discussion and investigations on the effect of wet deposition on corrosion attack, it may be said that the present material does not show any significant influence of the pH or SO_4^{2-} deposition rate in precipitation on the corrosion of steel. A slight influence of the SO_4^{2-} deposition rate in precipitation was observed in the case of zinc. This effect, which definitely seems to be only complimentary to the effect of SO_2 and chlorides, will be subject to a further analysis after completion of the set of data. It may also be mentioned that no data at all has been available for the NO_x pollution.

The special pollution situation at the test site Brevik should also be discussed. This site is located close to a cement factory with heavy cement dust fallout. This fact explains the extremely low corrosion attack at prolonged test periods. The results from the Brevik site also underlines the fact that a useful system of classification of the corrosivity of atmospheres cannot include extreme pollution conditions.

Time Dependence of Corrosion Rate

The corrosion rates for one, two, four, and eight years' exposure of steel at selected sites according to the classification in Table 3 show a decrease in the corrosion rate with time, which is at most sites marked after the first year (Fig. 2). On prolonged exposure, the decrease slows down.

The development of Eq 5, which contains the time parameter and both the SO_2 and chloride term, may thus be of great practical importance. The equation can be used for calculations of the corrosion attack for desired time periods. An example of this is given in Table 3, in which the differential corrosion rates at ten years' exposure have been calculated. This value may be used for estimation of the steady state corrosion rate. In the future, further efforts should be made to express the value of constant n in Eq 1 as a function of the climatic parameters.

For zinc, the decrease in the corrosion rate after the initial one year period is much less pro-

nounced (Fig. 3). In atmospheres polluted by SO_2 and/or chlorides, the decrease is only slight. From the sites in Fig. 3, only the Stend site with a very high amount of precipitation, shows a sharp decrease in corrosion attack. The reason for this has already been discussed.

For zinc the value of n in Eq 1 may be considered one and the corrosion attack is assumed to be linear. For predictive purposes, Eq 8 may be used if the pollution parameters are known. For assessment of the steady state corrosion attack from field exposures, one year corrosion data may serve as an orientation. For more reliable prediction, field exposures of two to four years are recommended.

Conclusions

The investigation permits the following main conclusions:

1. Exposure of steel and zinc specimens at 32 sites in Scandinavia shows that the pollution by SO_2 in urban and industrial areas and by chlorides in marine locations is of decisive importance for the corrosion rate.

2. The differences in the corrosion rate of steel and zinc at six rural sites in Southern Scandinavia are very slight despite the variations in other environmental parameters.

3. The development of a dose response function which expresses the time-dependence of the corrosion of steel and zinc as a function of both the SO_2 concentration and the chloride deposition rate may be of great practical importance.

4. The results may serve as a basis for a quantitative description of corrosivity classes in systems for the classification of the corrosivity of atmospheres.

5. Also, the corrosion rates from one year's exposure of standard specimens seem to give a useful indication of the corrosivity of the atmosphere.

6. Among the gaps in knowledge which should be the subject of further work are the elucidation of the influence of rain quality and NO_x levels. Also, the use of strictly controlled standardized methods for measurement of pollution and meteorological parameters, including the wet candle method for the assessment of the chloride deposition rate should be stressed. Adoption of such methods in a network of test sites covering a broad interval of pollutant levels might improve the quality of the present dose response functions.

Acknowledgment

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DISCUSSION

R. S. Humphery¹ (discussion question)—Please explain why one industrial site showed lower corrosion than any rural area.

V. Kucera (author's closure)—The low rate site was adjacent to a cement factory, and specimens were coated with thick high pH deposits.

Fred H. Haynie¹

Environmental Factors Affecting the Corrosion of Galvanized Steel

REFERENCE: Haynie, F. H., "Environmental Factors Affecting the Corrosion of Galvanized Steel," *The Degradation of Metals in the Atmosphere, ASTM STP 965*, S. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 282-289.

ABSTRACT: Galvanized steel samples are exposed for periods of up to 30 months at nine air monitoring sites in the St. Louis, MO area. Climatic and air quality data are recorded during the exposure periods and subjected to a rigorous evaluation to eliminate recording errors and to estimate missing values. Weight loss is used as the measure of zinc corrosion on the galvanized steel. The corrosion rate is evaluated with respect to (1) fluxes of pollutants (sulfur oxides, nitrogen oxides, oxidants, and particles) to the galvanized steel during both wet and dry periods, (2) temperature, and (3) amount of rainfall at Lambert Field (airport). Different definitions of when the galvanized steel was wet are evaluated to determine the most likely "critical relative humidity." A theoretical model of film buildup and dissolution is developed to explain how factors affect corrosion rates. Nonlinear and linear multiple regression techniques are used to determine the statistic cal significance of each factor.

KEY WORDS: galvanized steel, corrosion, rain solubility, pollutants, climate

From the Fall of 1974 to the Spring of 1977, the EPA conducted an air pollution modeling study in St. Louis, MO [1]. Nine of 25 continuous air monitoring sites were selected to study the effects of pollutants on eight types of materials [2]. Galvanized steel (hot-dipped A40) was one of the materials. A report of previous analysis was based on unvalidated pollution data and time-of-wetness estimates from Lambert Field relative humidity data [3]. The effect of rain was not considered. This paper presents the results of a more complete analysis of the corrosion of galvanized steel with respect to validated environmental data.

Theoretical Considerations

Many metals form corrosion product films as they corrode. These films tend to restrict the rate of corrosion. In general, the rate of corrosion is inversely proportional to the thickness of the corrosion product film (the rate controlled by diffusion through the film). When the film is insoluble and does not change structure with time, the corrosion-time function is parabolic $(c = \alpha \sqrt{t})$. Many metal corrosion products have solubilities that are proportional to their acidity. Thus, in very acid solutions, films are very thin and the resulting corrosion-time function is almost linear. In atmospheric exposures, there are many sets of environmental conditions in which these two mechanisms compete. The results are the empirically observed relationships, $c = At^n$, where the exponent *n* most often has a value between 0.5 and 1.0 [4,5].

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Theoretically, the amount of corrosion c is the sum of the metal accumulated in the corrosion product film F and the amount of metal solubilized from that film with time βt_w

$$c = F + \beta t_w \tag{1}$$

where t_w is time-of-wetness, and β is a solubilization rate, which is a function of acidic pollutant fluxes. The rate of film thickness growth in units of metal corroded is

$$dF/dt_w = \alpha/F - \beta \tag{2}$$

where α is a function of diffusivities through the film. Pollutants may also affect this coefficient. Under constant conditions (none of the variables changing with time), integration of Eq 2 yields

$$-\beta^2 t_w = \beta F + \alpha \ln(1 - \beta F/\alpha) \tag{3}$$

Substituting Eq 1 into Eq 3 and rearranging produces the transcendental equation

$$c = \beta t_w + \alpha (1 - \exp(-\beta C/\alpha))/\beta$$
(4)

which is equivalent to

$$c = \beta t_w + \alpha / (dc/dt_w) \tag{5}$$

When $\beta c/\alpha$ is large, $\exp(-\beta c/\alpha)$ approaches zero, and Eq 4 becomes

$$c = \beta t_w + \alpha/\beta \tag{6}$$

In polluted environments, galvanized steel exhibits this linear behavior after only a few months. In clean environments, there may be some observable curvature within the first year. Linear behavior indicates that the rate of formation of a film through electrochemical reaction and diffusion is equal to the rate of dissolution. Rain can dissolve the complex protective basic zinc carbonate film that forms on galvanized steel [6]. The solubility of zinc carbonate is proportional to the concentration of carbon dioxide (CO₂) in solution [7], which in turn is proportional to atmospheric levels of CO₂. The solubility of CO₂ in water decreases with increasing temperatures². In St. Louis, atmospheric CO₂ levels varied within a range of 300 to 550 ppm and were negatively related to temperature (ppm = $515 - 5.69 \times T^{\circ}$ C) [9]. If it is assumed that rain equilibrates with both the atmosphere and the galvanized steel specimens, a corrosion coefficient associated with clean rain can be calculated from these relationships.

Rain only falls on the upper side of specimens exposed at 30° C to the horizontal. Thus, the average effect of rain on a specimen is 0.5 cos 30° of that on one side of a horizontal surface. With this factor included, a theoretical corrosion coefficient from clean rain is calculated from zinc carbonate (ZnCO₃) solubility data and the temperature dependent CO₂ levels in St. Louis. The results are

$$C_R = 0.4 \, \min(128.8 - 1.42T)^{1/3} \exp\left[-42.2 + 3194/DP + 4.53\ln(DP)\right] \tag{7}$$

where

 C_R = galvanized corrosion due to clean rain, μm ,

DP = average dew point temperature, °K,

²Spence, J. W., Haynie, F. H., Stiles, D. C., and Edney, E. O., in this publication, pp. 282-289.

T = average air temperature, °C, and

rain = total rainfall during exposure, cm.

(For details of the theoretical derivation, see Footnote 2 in this volume.)

The acidity in rain can increase the corrosion rate, not only by increasing the solubility of the corrosion product film, but also by depolarizing the cathodic reaction. Thus, from the definition of pH and with stoichiometric ionic exchange, zinc corrosion in micrometers caused by acidity is 46 rain $\times 10^{-pH}$. For the average contribution to corrosion on the 30° specimens, a pH of 4.2 was assumed and the above relationship was multiplied by 0.5 cos 30°.

Zinc corrosion is also believed to be stoichiometrically proportional to the amount of sulfur trioxide (SO₂) deposited on the surface during periods of wetness [3]. With accumulated SO₂ expressed as μ g/cm² and corrosion as μ m, the theoretically calculated coefficient is 0.00143. Also, a monolayer of SO₂ can absorb on surfaces during periods of dryness.

Measurement and Data Analysis

Environmental Data

Hern et al. [10] describes the data collection and evaluation system for the environmental parameters at the nine sites. Subsequently, the resulting Regional Air Pollution Study (RAPS) data base was revised several times using better validation techniques. The portions of that data base used in this study are hourly averages of temperature, dew point, windspeed, wind direction, total oxidant, NO_x , SO_x , and 24-h total suspended particulate matter (TSP) samples. The validation process excludes from the data base those values that for one reason or another have a low probability of being correct. This increases the fraction of data that are missing that could possibly bias the calculation of long-term averages or total accumulations. A methodology is developed [11], to estimate these missing values using total system relationships and relationships between the system and climatological data from Lambert Field (an airport meteorological station located about 16 km (10 miles) northwest of the St. Louis central business district). Rainfall and its chemistry is not recorded at the exposure sites. Since rainfall was expected to be an important parameter, data from Lambert Field are used in this study.

Galvanized Steel Corrosion

Duplicate specimens were exposed for periods varying from 3 to 30 months with exposures started at each of the four seasons during the first year. The experimental procedure and exposure schedule are documented in an EPA report [2]. The results are 153 sets of duplicate weight loss data with site, exposure time, and initial exposure season as primary variables.

Analysis of Environmental Data

Although the methodology for analyzing the data has been previously reported [11], there are some differences that should be noted. First, a later version of the RAPS data base was used as an initial source. Second, time-of-wetness in this paper is defined differently. Thus, the relationship used to calculate relative humidity from temperature and dew point is based on data for dew points greater than 0° C. Third, deposition velocities are calculated from boundary layer theory rather than empirical relationships.

Time-of-wetness as previously defined is the time exceeding some critical relative humidity [11]. In this paper time-of-wetness is the time a critical relative humidity is exceeded and the dew point is greater than 0°C, plus any time the critical humidity is not exceeded and it is raining. This definition is more consistent with time-of-wetness data collected at four of the sites during the Fall of 1976 using instantaneous Atmospheric Corrosion Monitors [12]. For that

reason, a regression relating relative humidity to dew points above $0^{\circ}C$ and temperature is used to calculate relative humidity for each hour. This empirical relationship from table data is

$$RH = 100 \exp\{[-0.0722 + 0.00025(T + DP)][T - DP]\}$$
(8)

where RH is relative humidity, T is temperature, and DP is dew point, with the last two in $^{\circ}C$.

Deposition velocities are calculated from windspeed data. Windspeeds at tower height can be used to calculate windspeeds at specimen rack height using the relationship for rough surfaces [13]

$$V^{+} = 8.5 + 2.5 \ln(Z/e) \tag{9}$$

where V^+ is the dimensionless velocity, and z and e are the measuring height and roughness height, respectively. The rack height is about 3 m from the ground. At three of the sites the meteorological towers were 10 m while at the others they were 30 m. The average ground roughness height is arbitrarily assumed to be 0.1 m (a factor of 10 difference in this estimate affects the rack height windspeed estimate by less than 12%). Thus, the rack height windspeed is 0.75 times the windspeed at 30 m or 0.85 times the windspeed at 10 m.

From analogy with momentum transport, gases with a Schmidt number of approximately one that readily react at a surface have a deposition velocity of

$$u = V^{*2} / V_1 \tag{10}$$

where u is the deposition velocity, V^* is the friction velocity, and V is the average windspeed. The friction velocity is equal to $V\sqrt{f/2}$ where f is the friction factor. From boundary layer theory for smooth flat plates [14]

$$f = 0.03/(RE_L)^{1/7} \tag{11}$$

where $RE_L = LV/\nu$, L = length of surface over which the air flows, and ν is the kinematic viscosity of air (0.15 cm²/s). L is assumed to be the geometric mean of the panel dimensions ($\sqrt{10.2 \times 15.2} = 12.45$ cm). Thus

$$u = 0.35 V_{10}^{0.86} \tag{12a}$$

$$u = 0.31 \ V_{30}^{0.86} \tag{12b}$$

with u in cm/s and V_{10} and V_{30} in m/s.

Deposition velocities are calculated on an hourly basis and averaged over exposure periods. Because windspeeds are not normally distributed, the average deposition velocity is about 91% of the deposition velocity calculated from average windspeed for an exposure period.

Pollutant Accumulation

Hourly deposition velocities are multiplied by hourly pollutant concentrations to get hourly pollutant fluxes. These are summed over exposure periods for hours of wetness with different critical relative humidity criteria (75 to 90% in 5% intervals).

The surface of galvanized steel is expected to be wet when a corrosion product and contaminant saturated solution is at a temperature below that for which the saturated solution is in equilibrium with the ambient relative humidity. The equilibrium relative humidity for zinc sulfate is temperature dependent (94.7% at 5°C and 90% at 20°C) [8]. If zinc sulfate is the major soluble constituent on the surface, the definition of time-of-wetness should include the effect of temperature variation. From the two points, a linear relationship for critical relative humidity and temperature is $RH_c = 96.27 - 0.313 T$.

Average dew points are taken as indicators of solution temperatures and redefined critical relative humidities are calculated for each of the 153 sets of data. Calculated accumulations of SO_2 at 75, 80, 85, and 90% are then extrapolated to these critical relative humidities. These accumulations should provide a more theoretically consistent fit of the corrosion data than assuming a set relative humidity as a critical value.

Accumulations of TSP are calculated by multiplying total exposure time by average TSP by the terminal settling velocity for an assumed size distribution of coarse mode particles (for the upper side of 30° specimens).² Pollutant fluxes can be calculated by dividing accumulations by total time or time-of-wetness.

Statistical Analysis of Data

An initial regression is performed on the data to determine the degree of nonlinearity and relative significance of each of the factors. The form of the model was

$$\ln(C) = \sum a_i \ln(t_w) + \beta T + \sum \sigma_i P_i + RR$$
(13)

where C is amount of galvanized steel corrosion, t_w is time-of-wetness for different critical relative humidities, T is temperature, the P_i s are the pollutant fluxes, and RR is the rain rate (amount of rain/ t_w). Both forward and backward stepwise regressions are done.

Corrosion is linear with time. Temperature is negatively significant, and TSP, SO₂, and rain are positively significant. Ozone, NO₂, SO₄⁼ in TSP, and NO₃⁻ in TSP are not statistically significant.

Simple linear regressions of corrosion against time for each set of site-starting season data, in most cases, produce fits that account for better than 0.99 of the variability. The corrosion rates based on these slopes average 0.762 μ m/year with an estimated standard deviation of 0.118 μ m/year. The values ranged from a low of 0.553 μ m/year for a set started in Spring at a relatively clean site, to a high of 1.054 μ m/year for a set started in Winter at a relatively polluted site. Thus, environmental differences within a metropolitan area can nearly double the corrosion rate of zinc.

The data including the four significant variables (temperature, TSP, SO₂, and rain) are analyzed using multiple linear regression techniques in several ways. Corrosion rates are regressed against fluxes of pollutants and corrosion is regressed against accumulations of pollution. Data are divided into four sets corresponding to starting seasons to determine if there are significant differences in coefficients between starting seasons.

Based on statistically significant differences in regression coefficients, the data could be divided into two groups having different corrosion behavior characteristics: those with exposures started in Fall or Winter, and those with exposures started in Spring or Summer. This factor is introduced into the regression analysis of the total data set as a dummy variable; that is, one for the Fall or Winter and zero for the Spring or Summer.

Evaluation with Respect to Theory

Based on the initial analysis, the data can be evaluated with respect to three components that contribute to corrosion for two starting seasons. The observed negative effect of temperature can be explained by the theoretically expected effect of temperature on the solubility of zinc carbonate in rain. The SO₂ effect can also be theoretically explained. The coefficient for the effect of particles, however, cannot be calculated theoretically.

A wet deposition component to corrosion is theoretically calculated by adding the acidity effect of a 4.2 pH rain to the value for clean rain solubility calculated using Eq 7.

A theoretical SO₂ component is calculated by multiplying 0.00:43 times the accumulation of SO₂ expressed as $\mu g/cm^2$. This accumulation is calculated using the temperature, dependent definition for critical relative humidity, plus a monolayer per day to account for the amount that could be absorbed on the surface during periods of dryness. This monolayer absorption effect is equivalent to a corrosion rate of 0.047 μ m/year.

The accumulation of particles in mg/cm² was calculated as the Total Suspended Particulate Matter (TSP) concentration in μ g/m³, times the exposure, times a factor of 0.01133. This factor assumes that only the coarse mode fraction is deposited on the upper surface, that half of TSP is in the coarse mode, and the deposition velocity is 1.66 cm/s. The latter is the calculated average terminal settling velocity of a particle distribution with a mass median diameter of 10 μ m, a geometric standard deviation of 2, and an average density of 2 g/cm³.

The resulting linear model for corrosion of zinc is

$$C = a_0 + a_1 \mathrm{SO}_2 + a_2 R n_c + a_3 \mathrm{TSP}$$
(14)

where SO₂ is the theoretical component of corrosion in μ m attributable to SO₂ deposition, Rn_c is the theoretical component of corrosion in μ m attributable to rain deposition, and TSP is the calculated average coarse mode particle accumulation in mg/cm². Any of the a_i coefficients may be the same or differ between the two starting seasons. Thus, to evaluate this possibility, the dummy variable and the product of the dummy variable and each of the three factors should be included in a multiple linear regression analysis.

The results are given in Table 1.

Apparently, the starting season only affects the coefficient for the rain deposition component. Neither the season variable alone or the product of the season variable with the other variables have high probabilities of being different from zero.

Discussion

The coefficient for the SO_2 deposition component is not significantly different from one, which is a strong indication that the theoretically calculated effect is correct. The average effect in the St. Louis area during this study accounts for 29% of the corrosion on the samples started in the Fall or Winter and 33% of it for the samples started in the Spring or Summer.

The theoretical rain deposition effect is based on equilibrium calculations. Equilibrium will not be reached if the residence time for rain on the specimens is short with respect to reaction rate half-lives. In this case the coefficient would be expected to be less than one.

Another factor to consider is that the solubility of zinc carbonate only serves as a proxy for the

Variable	Units	Means	Coefficient a_i	Standard Error	t Statistic
Corrosion					
(intercept)	μm	0.854	-0.024		•
SO ₂ deposition	μm	0.255	0.958	0.087	10.97
Rain deposition	μm	0.798	0.269	0.070	3.85
Season \times rain					
deposition	μm	0.509	0.188	0.022	8.50
Particle					
accumulation	mg/cm ²	0.796	0.406	0.041	10.01
	-				

TABLE 1-Linear regression results for galvanized steel corrosion function.^a

"Fraction of variation explained by regression $R^2 = 0.9762$. Standard deviation of residuals = 0.0976. The probability that the *t* statistic indicates coefficient = 0 is < 0.0001 for all but the rain deposition variable. That probability is 0.0002.

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solubility of a much more complex corrosion product film that varies in structure with exposure to different environments. The basic zinc carbonate film may have different ratios of zinc oxide (ZnO) to $ZnCO_3$ as well as different levels of hydration. Starting exposures in Fall and Winter could favor the formation of a more soluble film. Higher CO_2 levels should favor a greater percentage of $ZnCO_3$, and lower temperatures should favor a higher level of hydration.

Rain deposition accounts for 33% of the corrosion of samples started in the Fall and Winter and only 24% of the corrosion of those started in Spring or Summer.

Calculated coarse mode particle accumulation was the major contributor to the corrosion of zinc in this study, accounting for 38% of the corrosion of the Fall-Winter started samples and 44% of the corrosion of the Spring-Summer started samples. The reaction of species within particles with zinc cannot account for the magnitude of this effect. For example, if ammonium acid sulfate were the reactive species, it would have to be 53% of the particle mass to stoichiometrically cause the observed contribution to corrosion. The percentage of sulfate in both fine and coarse modes combined is less than 20%, and most of that should be in the fine mode.

This strongly suggests that particles had a catalytic effect on corrosion. One possible mechanism is that soluble species, such as chlorides, lower the critical humidity for dew formation, thus increasing the fraction of time when the surface is wet.

The very low negative intercept indicates that the corrosion product film is very thin in St. Louis, where SO_2 levels are relatively high. In regions where SO_2 levels are low, positive linear regression intercepts should be obtained and nonlinear behavior should be observed during the early months of exposure.

Conclusion

Sulfur dioxide accumulation on zinc stoichiometrically reacts to form soluble zinc sulfate. The accumulation during periods of wetness and dryness can be calculated from windspeed, dew point, temperature, and SO₂ concentration data.

The accumulation of particles on upper surfaces is a major contributor to the corrosion of zinc, possibly by increasing the time of wetness.

Rain contributes significantly to the corrosion of zinc by dissolving the protective corrosion product film. The film structure and solubility may vary with the season in which exposures are started.

Ozone, oxides of nitrogen, sulfate, and nitrates in TSP are not statistically significant factors in the variability of corrosion of these specimens exposed in the St. Louis area.

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Atmospheric Corrosion in Maritime Industrial Atmospheres: Laboratory Research

REFERENCE: Knotková, D., Barton, K., and Tu, B. V., "Atmospheric Corrosion in Maritime Industrial Atmospheres: Laboratory Research," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 290-305.

ABSTRACT: An extensive testing program was carried out for studying the corrosion of steel and zinc in environments intended to model atmospheres containing SO_2 , SO_4^{2-} , sodium chloride (NaCl), and seawater. Both gaseous and droplet types of the corrosion stimulators were introduced into the system together, alternatively, or subsequently in graduated doses. The corrosion tests were performed in a cyclic mode. The weight losses, composition of corrosion products, and radiochemical detection of sulfates have been followed. Parallel stimulation of the steel and zinc atmospheric corrosion by the CI^- and SO_4^{2-} ions cannot be described by a simple relation. Further components of the reaction system participate in the control of the corrosion kinetics.

KEY WORDS: corrosion, accelerated corrosion tests, steels, zinc, sulfur dioxide, sulfates, chlorides, marine industrial atmospheres

The atmospheric corrosion of metals in polluted atmospheres is a serious problem of the present times. This problem is important for the following reasons:

1. The additional pollution beyond sulfur dioxide (SO_2) in the atmosphere, caused by industrial activity is sufficiently high that both the kinetics and the mechanism of the corrosion processes are affected.

2. The critical components within a number of products are intricate electronic systems that are sensitive to even slight corrosion effects occurring in slightly aggressive internal atmospheres, and these are greatly affected by pollution typical in such environments.

3. Emphasis is placed on the industrialization of the countries of the third world where the production plants are usually built in marine regions. The plants are, however, subjected to the effect of marine salinity and industrial air pollution often in tropical climate conditions.

The third case is the subject of our study. Certain plants have been built while industrializing the Vietnam Socialist Republic in marine regions, and a lot of these materials have been subjected to the effects of an industrial marine atmosphere. The importance of the solution of the Vietnamese problem is the fact that its coast is longer than 200 km and that most of the plants under construction are situated there.

The simultaneous effect of manmade and natural stimulators of atmospheric corrosion of metals and especially of sulfur oxides, sulfates, and chlorides can only be followed by difficult experiments based on natural exposures and the simultaneous measurement of the stimulator

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levels. The problem consists in the finding of localities with different levels of the combinations of the atmospheric components. As the knowledge of the accelerating functions of the atmospheric corrosion stimulator combinations is, however, important for the purpose of the evaluation of the corrosivity of actual atmospheres, for example, marine localities with simultaneous industrial emissions, the problem can best be solved by laboratory simulation of the combined effects. The detailed mathematical modeling of the stimulation effects of sulfur oxides on the atmospheric corrosion of metals [1,2] and the studies concerning the mechanism and the kinetics of atmospheric corrosion in the presence of chloride deposition [3] can be taken as a basis. Only some studies [4-6] are concerned with the problems of both the stimulator groups and present basic information on the influence of their combinations on the kinetics of corrosion.

It is known from studies on the kinetics of the atmospheric corrosion of "nonpassive" metals that the mechanism of the stimulator effect on the reaction system controls process kinetics. From this point of view, the participation of the stimulating anions in the atmospheric corrosion process is usually divided as follows:

1. The mechanism whereby the anions return back into the solution by hydrolysis of the primary corrosion products. The typical representative of metal corroding by this mechanism is iron and its alloys, and especially, carbon steels.

2. The mechanism involving a direct or secondary formation of hydroxide salts with a relatively stable bond of stimulating anions. Some nonferrous metals, for example, zinc, copper, cadmium, and so forth, corrode in this mode.

The specific mechanism of the stimulating anion's participation in atmospheric corrosion is clearly demonstrated by the different kinetics of the processes of both the types of stimulators. The processes involving resolution of anions in the system are usually about ten times faster than processes with a stable bond of anion in corrosion products [7]. For these reasons, carbon steel and zinc have been selected as representatives of metals for both the reaction types.

Plan of Experiments

In the laboratory simulation of the effects of the atmospheric corrosion stimulators the basic problem always consists in their proportioning, so that the natural mechanism and the kinetics of their introduction into the reaction system are simulated and that the proportioning itself is experimentally controllable without excessively high demands made on the proportioning technique and on the required precision.

With regard to the mentioned requirements, the techniques based on dosing the simulator on the surface of the individual specimens by a micropipette or spray have been rejected in the present study. Use of standard laboratory equipment for routine "accelerated" tests of atmospheric corrosion has been the basis of the present work. A survey of this type of equipment and of its working characteristics is presented in Table 1.

The following isolated effects were available for the test program.

(a) the effect of distilled water aerosol with condensation of water vapor as a reference corrosive environment without the effect of the stimulators,

(b) condensation of water vapor in the presence of SO_2 as a reference environment with the stimulation by sulfur oxides,

(c) the effect of an aerosol of a 1% sodium chloride (NaCl) solution with a chloride deposition rate of 600 g m⁻² d⁻¹ to 630 g m⁻² - d⁻¹,

(d) the effect of an aerosol of artificial seawater with a deposition rate of chlorides of 600 to 630 g m⁻² $- d^{-1}$, and

(e) supplementary sprays of a solution of sodium sulfate (Na_2SO_4), NaCl, or artificial seawater, or both.

				Technical Variables of Environment
Type and Designation of Equipment	Principle of Environment Generation	Temperature, °C	Relative Humidity, %	Kind, Range, and Mode of Corrosion Stimulator Proportioning
Condensation chamber of Czechoslovak production KK 260	condensation of water steam	40	100	A-without stimulators B-SO ₂ liberated by evaporation from the solution into distilled water at the chamber bottom of the solution of sulfurous acid is cycli- cally carried; the starting intermittent concentration is 2.0 ± 0.2 SO ₂ , 1 ⁻¹ in the testing space C-the same as B and the spray by 100- or 200-mg NaCl · m ⁻² · d ⁻¹ or by corresponding quantity of chlorides of aptificial seawater D-the same as B and the starting nonceurring spray by 500, 1000, or 2000-mg NaCl · m ² or corresponding quantity of artificial
Aerosol chamber Weiss system S 400, WK 400 type	the atomization of water or solu- tion	35	95 to 100	 scawater culorides A—without stimulators B—600 to 630-mg NaCl · m⁻² · d⁻¹ on sample vertical surfaces C—ditto in the form of artificial scawater chlorides D—the same as C and the spray by 150- or 300-mg SO₄⁻² · m⁻² · d⁻¹ in the form of Na₂SO₄ solution E—the same as C and intermittent additional spray by 1000-mg SO₄⁻² in the form of Na₂SO₄ solution
NOTES: 1% solution of NaC	l aerosoled and aeroso	led solution of arti	ficial seawater/	NaCl 23g · 1 ⁻¹ , MgCl ₂ 6g · 1 ⁻¹ , KCl Ig · 1 ⁻¹ , CaCl ₂ Ig · 1 ⁻¹ .

TABLE 1–Testing equipment used in this study.

With regard to the current test program, the isolated effects were combined according to the scheme b/c, b/d, b/e, c/e, d/e, that is, either with the nonrecurring effect of the first of the pairs of the stimulators at the beginning of the test cycle or by the alternating effect of both factors, that is, either by the alternating location of samples in b and d environments or by the supplementary effect of the sprays (e) on samples located in b or d environments. The list of experiments is given in Table 2.

Experiments and the Evaluation of Tests

Corrosion was observed on carbon steel and commercial zinc, which were representatives of structural metals and, at the same time, the metals that represent two different mechanisms of metal corrosion in polluted atmospheres.

The chemical composition of metals in percent was as follows:

• steel: carbon maximum 0.07, manganese maximum 0.40, aluminum minimum 0.025, phosphorus maximum 0.025, sulfur maximum 0.025, copper maximum 0.07.

• zinc: lead 0.55 and iron 0.015.

The samples of metals of 80 by 30 by 1 mm dimensions were pickled before the test, that is, steel in 18% hydrochloric acid (HCl) and zinc in 5% acetic acid. The initial mass of the samples was determined with the accuracy of 0.1 mg.

The various tests shown in Table 2 were carried out as one day cycles; the samples were always exposed in the test chamber for the period of 8 h and in normal condition in the laboratory for 16 h at the temperature of approximately 20° C and relative humidity of 60 to 70%.

The samples were evaluated after the test by determining the changes of appearance, mass, by use of microscopic (SEM), analytical, radiochemical, and phase analysis techniques.

The JEOL-JSM-25S electron microscope was used for the electron microscopic evaluation. The analytical determination concerned the content of the corrosion stimulators in the corrosion products. The X-ray microanalysis, chemical analysis, and X-ray macroanalysis (Linc MECA 10-44 equipment) were selected for the analysis of the corrosion products. The autoradiography of the sulfate nests was carried out by ${}^{35}SO_4^{2-}$ exchange in the corrosion layer.

Test Results

Weight Losses

The results of the corrosion tests in the form of a survey of the weight losses for steel and zinc are stated in the enclosure.

For simplification we have processed the results in the form of the differential corrosion rates for the starting period of the corrosion and for the period during which the corrosion rate is stabilized. We have furthermore stated the relative corrosion rates with regard to the corrosion rates in the basic-comparison environments. The concerned surveys are shown in Tables 3 through 6. Parts of the results are shown in the relevant graphs (Table 7).

Morphology and Composition of Corrosion Products

The evaluation of the appearance and evaluation with the use of the SEM leads to the conclusion that rather fine-grained corrosion products with occasional mushroom-like formation grow on the steel samples in the condensation chamber with SO_2 . In the seawater aerosol environment rather coarse needle-like formations are apparent; if the NaCl solution is sprayed, the needles are better developed. The influence of chlorides predominates in combined corrosion environments according to the evaluation of the corrosion product morphology.

The mixture of the needle-like and amorphous corrosion products occurs also on zinc. Amor-

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					Test	Mode in One-D	ay Cycle	
			Ę		Ex ₁ Enclos	posure in ed Chamber	Time of Exposure in Normal Conditions (20°C,	f, maril
		Tectino	Ies	с Епунопшенс	Time	Temnerature	Relative	Exposure
Number	Code	Equipment	Pollution	Introduction Method	h h	°C	humidity)	(Cycle)
1	WK-1a	WK-S400	without pollution	spray by distilled water 2 to 9 3 m in 1 h	×	35 ± 1	16	30
2	WK-1b	:	1% NaCl	continuous spray by 1 % NaCl	8	35 ± 1	16	10
e	WK-1c	:	seawater	continuous spray	2.5	35 ± 1	21.5	10
4	WK-1d	:	seawater	spray, 2 to 9.3 min in 1 h	×	35 ± 1	16	10
S	WK-2a	WK-S400	seawater + $1000 \text{ mg} \cdot \text{m}^{-2}$ SO ²⁻	as WK-1d + single-dosing spray by Na ₂ SO ₄ solution	×	35 ± 1	16	30
Q	WK-2b(150)	:	50 mg · m ⁻² 150 mg · m ⁻² SO ^{2−}	as WK-1d + daily spray by Na ₂ SO ₄ solution	×	35 ± 1	16	30
٢	WK-2b(300)	:	seawater + $300 \text{ mg} \cdot \text{m}^{-2}$ SO ²⁻	:	æ	35 ± 1	16	30
œ	KK-la	KK -260	without pollution	single-dosing spray bv NaCl solution	×	40 ± 2	16	30
6	KK-1b(500)	KK-260	NaCl 500 mg · m ⁻²	single-dosing spray by NaCl solution	x	40 ± 2	16	30
10	KK-1b(1000)	:	NaCl 1000 mg · m ⁻²		8	40 ± 2	16	30
II	KK-1b(2000)	:	NaCl 2000 mg · m ⁻²	:	×	40 ± 2	16	30
12	KK-1c(500)	KK-260	seawater corre- sponding to the fall-out of chlo- rides 500 mg · m ⁻² Nacti	single-dosing spray by scawater	œ	40 ± 2	16	30
13	KK-1c(1000)	:	1000 mg · m ⁻² NaCl	:	×	40 ± 2	16	30
14	KK-1c(2000)	:	2000 mg · m ⁻² NaCl	F	×	40 ± 2	16	30

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15	KK-1d	:	$2 \text{ mg} \cdot 1^{-1} \text{ SO}_2$	daily portion of 22.5-mL ۲۵٫, H.SO.	8	40 ± 2	16	30
16	KK-2a(500)	:	$SO_2 + NaCl$	as KK-1d + single dosing	æ	40 ± 2	16	30
17	KK-2a(1000)	:	$SO_2 + NaCl1000 mg·m-2$		80	40 ± 2	16	30
18	KK-2a(2000)	:	$SO_2 + NaCl 2000 mo \cdot m^{-2}$	*	×	40 ± 2	16	30
19	KK-2b(500)	KK-260	So $_{2}$ + seawater corresponding to the fall-out of chlorides 500 mg \cdot m ⁻² Norci	as KK-ld + single-dosing spray by sea water	œ	40 ± 2	16	30
00	K K-2P(1000)	•		*	×	40 + 2	16	00
51	KK-2b(2000)	:	2000 mg · m - 2 NaCl	**	o oc	40 ± 2	16	30
22	KK-2c(100)	:	$SO_2 + NaCl - 100 me \cdot m^{-2}$	as KK-1d + daily spray by NaCl solution	8	40 ± 2	16	30
23	KK-2c(200)	:	$SO_2 + NaCl - 200 mg \cdot m^{-2}$	-	æ	40 ± 2	16	30
24	KK-2d	:	SO_2 + seawater corresponding to fall-out of chlorides of 100 mg \cdot m ⁻² NaCI	as KK-1d + daily spray by scawater	×	4 0 ± 2	16	30
25	WK-KK-1(3c)	WK-S400 + KK-260	chlorides and SO ₂	precorroding as WK-1d (3 cvcles), exposure in KK-1d	8	35 ± 1	16	30
26	WK-KK-1(6c)	:	:	pre-corroding 6 cycles	8	35 ± 1	16	30
27	WK-KK-1(12c)	:	:	pre-corroding 12 cycles	8	35 ± 1	16	30
28	WK-KK-2(1:4)	:	:	alternating exposures in two	œ	35 ± 1	16	30
				WK-1d and KK-1d WK-1d and KK-1d 1 cycle WK-1d A moloc KK-1d		40 ± 1		
29	WK-KK-2(1:1)	:	÷	I cycle WK-1d + 1 cycle KK-1d		:	16	30
30	WK-KK-2(4:1)	:	:	4 cycles WK-1d + 1 cycle KK-1d		:	16	30

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	Experiment	Differential Corrosion Rate, mg · dm ⁻² · d ⁻¹ Interval, Days of Exposure				
Number	Code	0-5	5-10	20-30		
1	WK-1a	12.0	9.2	29.4		
4	WK-1d	136.8	123.2	174.0		
5	WK-2a	144.0	208.1	266.4		
6	WK-2b(150)	240.0	284.1	211.8		
7	WK-2b(300)	146.8	91.6	135.2		
8	KK-1a	8.4	4.4	4.6		
9	KK-1b(500)	89.2	98.0	6.6		
10	KK-1b(1000)	110.4	122.4	36.4		
11	KK-1b(2000)	140.0	155.2	40.2		
12	KK-1c(500)	136.0	108.0	26.8		
13	KK-1c(1000)	140.4	203.2	34.0		
14	KK-1c(2000)	176.0	228.0	22.0		
15	KK·1d	254.8	228.0	212.4		
16	KK-2a(500)	221.2	290.0	201.6		
17	KK-2a(1000)	265.6	278.4	240.2		
18	KK-2a(2000)	216.0	303.2	233.4		
19	KK-2b(500)	195.6	284.4	202.8		
20	KK-2b(1000)	250.8	370.4	197.8		
21	KK-2b(2000)	223.2	295.6	227.4		
22	KK-2c(100)	336.0	375.2	188.4		
23	KK-2c(200)	394.8	475.6	196.2		
24	KK-2d	380.8	399.2	383.8		
25	WK-KK-1(3c)	589.2	361.2	308.6		
26	WK-KK-1(6c)	549.2	479.2	160.6		
27	WK-KK-1(12c)	666.8	386.0	389.2		
28	WK-KK-2(1:4)	293.2	402.8	338.6		
29	WK-KK-2(1:1)	180.0	556.0	235.6		
30	WK-KK-2(4:1)	176.0	215.2	200.4		

TABLE 3-Differential corrosion rates of steel.

phous or products with low-developed crystallinity occur at the presence of SO_2 or sulfates. From the morphology point of view, the effect of sulfates is greater than in the case of corrosion products on steel.

The results of the microanalysis show the relatively low content of chlorides in the layer of corrosion products, which proves a greater water solubility of the corrosion products and their dissolution from the layer.

The phase analysis was carried out only on selected samples. Rust on steel samples from nonpolluted environments and from environments with SO₂ with accompanying sprays of NaCl contained the α -FeOOH and iron oxide (Fe₃O₄) phases.

In samples from the chamber with the seawater aerosol and with accompanying effects the β -FeOOH, α -FeOOH and Fe₃O₄ were always found. The portion of the β -FeOOH was most evident in rusts of samples without the accompanying effect of the SO₂ (SO₄²⁻) stimulator.

The corrosion products on zinc form intricate mixtures. We have not been successful in identifying some of the components.

The $ZnSO_4 \cdot 3Zn(OH)_2 \cdot 4H_2O$ phase predominates in corrosion products from the condensation chamber with SO_2 in spite of the application of the chloride containing sprays. Zinc chloride, hydroxide ($Zn_5(OH)_8Cl_2$) and zinc oxide (ZnO) are formed in the presence of the seawater

Experiment		Corrosion Rate Rations			ons
Number	Code	0-5 I	Days	20-30	Days
4	WK-1d	1		1	
5	WK-2a(1000)	1.0)52	1.5	31
6	WK-2b(150)	1.7	/54	1.2	17
7	WK-2b(300)	1.0)73	1.7	77
8	KK-1a	1		1	
9	KK-1b(500)	10.6	519	1.4	34
10	KK-1b(1000)	13.1	142	7.9	13
11	KK-1b(2000)	16.6	666	8.7	39
12	KK-1c(500)	16.1	190	5.5	83
13	KK-1c(1000)	16.7	714	7.3	91
14	KK-1c(2000)	20.952		4.7	82
15	KK-1d	1		1	
16	KK-2a(500)	0.868		0.9	49
17	KK-2a(1000)	1.042		1.1	30
18	KK-2a(2000)	0.847		1.0	98
19	KK-2b(500)	0.767		0.9	54
20	KK-2b(1000)	0.984		0.9	31
21	KK-2b(2000)	0.8	875	1.0	70
15	KK-1d	1		1	
22	KK-2c(100)	1.3	318	0.887	
23	KK-2c(200)	1.5	549	0.923	
24	KK-2d(100)	1.4	494	1.803	
15	KK-1d	1		1	
25	WK-KK-1(3c)	2.3	312	1.4	52
26	WK-KK-1(6c)	2.	155	0.7	/56
27	WK-KK-1(12c)	2.0	616	1.8	332
15	KK-1d	1		1	
4	WK-1d		1		1
28	WK-KK-2(1:4)	1.150	2.143	1.594	1.945
29	WK-KK-2(1:1)	0.706	1.315	1.109	1.354
	WK-KK-2(4:1)	0.690	1.286	0.943	1.151

TABLE 4-Relative corrosion rates of steel.

aerosol. We have not been successful in identifying the corrosion products on zinc after alternating exposure in the condensation chamber with SO_2 and with the seawater aerosol.

The results of the autoradiographical evaluation of the sulfate nests were probably affected by the macrostructure and thickness of rust layers, which were very different. In spite of this fact, it can be assumed of the results that the localization of the sulfate nests occurs in combined environments with a joint action of chlorides and sulfates.

A preliminary exposure in a chloride environment has a positive influence on the formation of the sulfate nests and especially on their density. The concentration of sulfates in the original chloride agglomerations cannot be eliminated. A permanent parallel effect of chlorides prevents the sulfate nests formation and localization.

Some characteristic layers of corrosion products are evident in the SEM photographs (Fig. 1). The differences in the topography of the sulfate nests are evident in Fig. 2.

Kinetics of Corrosion at Various Variants of Test

The results of the corrosion tests of the groups of experiments corresponding to various combinations of partial effects will be characterized in detail in the following sections.

	Experiment -	Differe I Interva	ential Corrosion mg · dm ⁻² · d ⁻ al (Time of Ex	n Rate,
Number	Code	0-5	5-10	20-30
1	WK-1a	2.4	2.4	0.6
4	WK-1d	18.8	9.2	8.0
5	WK-2a	21.2	23.8	19.0
6	WK-2b(150)	21.2	10.4	27.2
7	WK-2b(300)	21.6	32.8	50.8
8	KK-1a	7.2	5.6	0.2
9	KK-1b(500)	8.8	1.6	0.6
10	KK-1b(1000)	14.4	1.6	0.4
11	KK-1b(2000)	17.2	8.8	0.6
12	KK-1c(500)	7.0	1.0	0.8
13	KK-1c(1000)	10.0	1.2	0.2
14	KK-1c(2000)	12.4	1.6	1.8
15	KK-1d	17.2	16.0	16.2
16	KK-2a(500)	11.4	6.6	10.6
17	KK-2a(1000)	17.8	12.6	17.6
18	KK-2a(2000)	18.0	9.4	17.0
19	KK-2b(500)	11.0	4.2	16.5
20	KK-2b(1000)	15.6	10.0	13.3
21	KK-2b(2000)	13.0	5.0	18.4
22	KK-2c(100)	14.8	9.6	17.2
23	KK-2c(200)	13.6	12.0	15.2
24	KK-2d	14.4	8.8	17.2
25	WK-KK-1(3c)	28.8	8.0	10.6
26	WK-KK-1(6c)	29.4	6.4	15.2
27	WK-KK-1(12c)	38.4	3.2	11.6
28	WK-KK-2(1:4)	20.0	11.2	11.8
29	WK-KK-2(1:1)	16.8	15.2	14.8
30	WK-KK-2(4:1)	17.4	8.8	17.2

 TABLE 5—Differential corrosion rates of zinc.

Corrosion of Steel and Zinc in Basic Testing Environments

The basic testing environments were pure condensation chamber and a condensation chamber with SO_2 , a Weiss aerosol generating chamber with distilled water, and with aerosols of artificial seawater.

It is evident from the corrosion curves (Figs. 1 and 2) that both environments are highly aggressive in the presence of the respective corrosion stimulators; the dependence of corrosion with time was generally linear and only the rate of zinc corrosion in artificial seawater aerosol decreased slightly with longer exposure. These results imply that these standard model environments generate a different corrosion process from natural conditions, except for cases involving extremely high levels of pollution.

The environment of the condensation chamber with SO_2 affects both metals more aggressively than the environment of the aerosol chamber with artificial seawater.

Corrosion of Steel and Zinc Affected by Chlorides

The contamination of both steel and zinc surfaces by NaCl, as well as by artificial seawater, greatly accelerates the corrosion in a wet environment. A more important acceleration of the steel corrosion by artificial seawater mentioned in the literature has been found in the initial period. A reduction of pH of the surface electrolyte after the hydrolysis of the admixture salts,

	F	Co	Corrosion Rate Ratios			
Number	Code	0-51	Days	20-30	Days	
4	WK-1d	1		1		
5	WK-2a(1000)	1.1	27	2.3	75	
6	WK-2b(150)	1.1	27	3.4	-00	
7	WK-2b(300)	1.1	48	6.3	50	
8	KK-1a	1		1		
9	KK-1b(500)	1.2	22	3.0	00	
10	KK-1b(1000)	2.0	00	2.0	00	
11	KK-1b(2000)	2.3	88	3.0	00	
12	KK-1c(500)	0.9	70	4.0	00	
13	KK-1c(1000)	1.3	1.388		00	
14	KK-1c(2000)	1.722		9.0	00	
15	KK-1d	1		1		
16	KK-2a(500)	0.622		0.6	54	
17	KK-2a(1000)	1.034		1.0	086	
18	KK-2a(2000)	1.046		1.049		
19	KK-2b(500)	0.639		1.018		
20	KK-2b(1000)	0.8	389	0.8	320	
21	KK-2b(2000)	0.7	755	1.1	35	
15	KK-1d	1		1		
25	WK-KK-1(3c)	1.6	574	0.654		
23	KK-2c(200)	0.7	790	0.938		
24	KK-2d(100)	0.8	337	1.061		
15	KK-1d	1	1		0.654	
25	WK-KK-1(3c)	1.6	1.674		54	
26	WK-KK-1(6c)	1.7	1.6/4		938	
27	WK-KK-1(12c)	2.2	232	0.7	716	
15	KK-1d	1		1		
4	WK-1d		1		1	
28	WK-KK-2(1:4)	1.162	1.063	0.728	1.475	
29	WK-KK-2(1:1)	0.976	0.893	0.913	1.850	
30	WK-KK-2(4:1)	1.011	0.925	1.061	2.150	

 TABLE 6—Relative corrosion rates of zinc.

 TABLE 7—Corrosion losses.

		C	orrosion Los Cyclic E	ses∕mg•dm xposure	- 2
Number	Experiment Code	5	10	20	30
	ST	TEEL SPECIM	IENS		
1	WK-1a	60	106	280	574
2	WK-1b	1212	3066		• • • •
3	WK-1c	256	734		
4	WK-1d	684	1300	2860	4600
5	WK-2a	720	1760	6696	9360
6	WK-2b(150)	1200	2620	6332	8450
7	WK-2b(300)	734	1232	5102	6454
8	KK-1a	42	64	164	210
9	KK-1b(500)	446	936	1782	1848
10	KK-1b(1000)	552	1164	2220	2584
11	KK-1b(2000)	700	1476	2886	3288
12	KK-1c(500)	680	1220	2152	2420
13	KK-1c(1000)	702	1718	2568	2908

		(Corrosion Los Cyclic I	sses/mg · dn Exposure	n ⁻²		
Number	Experiment Code	5	10	20	30		
		STEEL SPECIN	4ENS				
14	KK-1c(2000)	880	2020	3580	3800		
15	KK-1d	1274	2472	5190	7314		
16	KK-2a(500)	1106	2556	5544	7560		
17	KK-2a(1000)	1328	2720	5342	7744		
18	KK-2a(2000)	1080	2596	5346	7680		
19	KK-2b(500)	987	2400	5068	7096		
20	KK-2b(1000)	1000	2852	5204	7182		
21	KK-2b(2000)	1116	2594	5452	7726		
22	KK-2c(100)	1680	3556	6214	8098		
23	KK-2c(200)	1974	4352	7258	9220		
24	KK-2d	1904	3900	6586	8416		
25	WK-KK-1(3c)	2946	4752	6900	9986		
26	WK-KK-1(6c)	2746	5144	8380	9986		
27	WK-KK-1(12c)	3334	5264	8676	12568		
28	WK-KK-2(1:4)	1466	3480	6600	9986		
29	WK-KK-2(1:1)	900	3680	6844	9200		
30	WK-KK-2(4:1)	880	1956	5982	7986		
ZINC SPECIMENS							
1	WK-1a	12	24	34	40		
2	WK-1b	84	289				
3	WK-1c	28	52				
4	WK-1d	94	140	250	330		
5	WK-2a	106	225	500	690		
6	WK-2b(150)	106	158	296	568		
7	WK-2b(300)	108	272	726	1234		
8	KK-1a	36	64	72	74		
9	KK-1b(500)	44	52	56	62		
10	KK-1b(1000)	72	80	84	88		
11	KK-1b(2000)	86	130	142	148		
12	KK-1c(500)	35	40	44	52		
13	KK-1c(1000)	50	56	66	68		
14	KK-1c(2000)	62	70	88	106		
15	KK-1d	86	166	308	470		
16	KK-2a(500)	55	88	224	330		
17	KK-2a(1000)	89	152	264	440		
18	KK-2a(2000)	90	137	280	450		
19	KK-2b(500)	55	76	255	420		
20	KK-2b(1000)	78	128	269	402		
21	KK-2b(2000)	65	90	216	400		
22	KK-2c(100)	74	122	232	404		
23	KK-2c(200)	68	128	242	394		
24	KK-2d	72	116	232	404		
25	WK-KK-1(3c)	140	180	256	362		
26	WK-KK-1(6c)	147	179	230	382		
27	WK-KK-1(12c)	182	198	264	380		
28	WK-KK-2(1:4)	100	156	256	374		
29	WK-KK-2(1:1)	84	160	280	428		
30	WK-KK-2(4:1)	87	131	228	400		

TABLE 7—Continued.

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FIG. 1—Electron micrographs of corroded surfaces of steel and zinc: (a) experiment WK-1d, 30 cycles (\times 1000)—(steel), (b) experiment KK-1d, 30 cycles (\times 700)—(steel), (c) experiment KK-2b(1000). 30 cycles (\times 2000)—steel, (d) experiment KK-2c(100). 30 cycles (\times 700)—steel, (e) experiment KK-1d, 30 cycles (\times 700)—(zinc), (f) experiment KK-2c(200), 30 cycles (\times 700)—(zinc).

and especially of magnesium chloride $(MgCl_2)$, is effective for a limited period of time only in the case of a nonrecurring dosing. In the case of zinc, the NaCl, even though dosed in a nonrecurring mode, proved to be more active during the whole time period of the test.

Influence of Sulfates on Steel and Zinc Corrosion in Aerosol Chamber with Artificial Seawater Mist

Because of the techniques used, SO_4^{2-} was applied on the sample surfaces by a spray of Na₂SO₄ solution, and this application apparently affected the test result. The acceleration of the

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FIG. 2—Distribution of sulfate nests in rust layer (time of exposure, 30 cycles): (a) experiment KK-1d (A), (b) experiment KK-2a(500) (B), (c) experiment KK-2a(1000) (C), (d) WK-KK-2(1:4) (A), (e) WK-KK-2(1:1) (B), and (f) WK-KK-2(4:1) (C).

zinc corrosion is out of line with further series of tests. The effect of the steel corrosion stimulation was low when compared with the applied doses on the surfaces. The properties of the surface electrolytes were modified when compared with the conditions in actual environments. This problem will be dealt with further in the discussion.

Combined Effect of Sulfates and Chlorides in the Condensation Chamber with SO₂

The nonrecurring, as well as the daily application of NaCl and artificial seawater on the surfaces of the zinc specimens exposed to the environment of the condensation chamber with SO_2 , resulted in a deceleration of the corrosion rate that was more apparent in the case of application of artificial seawater, which occured mostly at the beginning of the exposure. The effect of the periodically introduced chlorides is not expressive in both the steady state and during the whole period of their introduction. A nonrecurring contamination of the steel surface by chlorides in the very aggressive environment of the condensation chamber with SO_2 is not very important from the kinetics point of view. A periodical contamination of the steel surfaces represents an acceleration of the corrosion rate, which is more apparent in the case of seawater application.

Influence of Combined Effect of Both Types of Polluted Model Environments

A combined effect of both environments was achieved by the alternating exposure in both chamber types as well as by the preliminary exposure in the aerosol chamber with artificial seawater before the exposure itself in the condensation chamber with SO_2 . This series of experi-

ments has shown a different effect of the combination of the corrosion stimulators for both metals.

Corrosion of steel samples initially corroded in the chamber with the seawater aerosol showed, during the starting period, the highest values of corrosion rate exceeding the total of corrosion rates attained in the individual environments. This effect disappeared at the end of the exposure period. The cause is found in the activity of H^+ ions in the surface electrolyte at the beginning of the exposure in the condensation chamber with SO₂, as well as in the variation of the frequency and the extension of the period of the salt agglomeration generation on the steel surface. The autoradiography has indicated the possibility of ion exchange processes between both stimulators in the agglomeration.

Corrosion rates corresponding to the sum of the partial contributions of the individual environments have been attained by the alternating exposure of steel in both chambers. In the case of zinc, the preliminary corrosion in the chamber with the seawater aerosol, as well as the alternating exposure in both the testing environments, reduced the effect of SO_2 . Both effects are evident in the graphs.

Discussion of the Results

In general, it must be stated that the parallel stimulation of the steel and zinc atmospheric corrosion by the Cl⁻ and SO_4^{2-} ions cannot be described by a simple relation, which would define the dependence of the kinetic parameters of the process and their admission into the components of the reaction system. The main reason consists in the existence of further components of the reaction system that participate in the control of the corrosion kinetics, that is, especially the following:

• The activity of H⁺ ions in the surface solution of electrolyte and at the reaction boundary surface differentiated according to the topochemical character of the anode and cathode parts of the corrosion process itself.

• After a very short induction period, layers of corrosion products develop that have the capability of bonding anions because of their chemical properties. These components control the overall rate of the process.

The importance of the activity of the H⁺ ions allows for the remarkably different initial courses of the iron and zinc corrosion during the introduction of SO_4^{2-} into the system, either in the form of gaseous SO_2 , on the assumption of a quick oxidation to SO_4^{2-} in the redox-systemmetal, solution of electrolyte, or in the form of the Na₂SO₄ solution. In the former case, higher activity of H⁺ in the surface solution of electrolyte is a direct consequence of the H₂SO₄ generation by the oxidation of SO₂ in solution as indicated below

$$H_2O + SO_2 + \frac{1}{2}O_2 \longrightarrow H_2SO_4$$

Also the hydrolysis of previously applied sulfates generates H^+ , especially in the case of iron.

However, if SO_4^{2-} is introduced in the form of the sodium sulfate (Na₂SO₄) solution, an increase of the pH value is, on the contrary, apparent as the result of the generation of a very stable solution of NaOH

$$Na_{2}SO_{4} \longrightarrow 2Na^{+} + SO_{4}^{2-}$$

$$Me_{+} + SO_{4}^{2-} \longrightarrow MeSO_{4} + 2e$$

$$\frac{1}{2}O_{2} + H_{2}O + 2e \longrightarrow 2OH^{-} \longleftarrow$$

The correctness of this concept follows from the apparently lower initial rate of steel corrosion by the introduction of Na_2SO_4 through a partial passivation processing in contrast to the effect of an equivalent amount of SO_2 and also from an opposite tendency characteristic for zinc. An increased alkalinity of the electrolyte solution after the introduction of Na_2SO_4 may cause the generation of soluble hydroxy complexes of zinc resulting in displacing the process beyond the sphere of the real corrosion process in environments with significant SO_2 contents.

The importance of the activity of the H⁺ ions is proved by the differences caused by the introduction of Cl⁻ in the form of NaCl solution or artificial seawater. Even in this case, the capability of the hydrolyzable components of artificial seawater, especially MgCl₂ and calcium chloride (CaCl₂), to regulate the pH of the surface electrolyte to values lower than is possible in experiments with the NaCl solution is apparent. The increased stimulation of the zinc corrosion after exposure to the NaCl solution in comparison with the solution of artificial seawater is the result [8]. After the formation of the layers of solid corrosion products, their properties control the kinetics of the process. In may be assumed that, depending on the concentration of Cl^{-} and SO_4^{-} , the properties of the layers became progressively stabilized so that they act as a regulator of the entire reaction system. The steady state, characterized by the activity of H⁺, Cl⁻, and SO_4^{2-} at the reaction boundary caused by the adsorption, desorption properties of products, and the capability of bonding Cl⁻ and SO_4^{2-} in more or less insoluble or hydrolyzable compounds or both is evident. Apparent differences evident during the starting period, which can be attributed to the parallel and individual activities of Cl^- and SO_4^{2-} and even H^+ , are removed, and the stabilized properties of the corrosion products become the controlling factor. The kinetics of the process are controlled by the type and concentration of the stimulator materials according to the following scheme



The corrosion products liberate more ions capable of reaction for the corrosion process itself at a higher concentration of the stimulator in the system. This regulating ability of the corrosion products is especially apparent in the case of iron. Zinc is characterized by a nonexpressive inhibition effect of the Cl⁻ ions, that is, mainly in the case where the exposure in an environment with the stimulation effects of SO_4^{2-}/SO_2 was preceded by the formation of a layer of corrosion products containing hydroxy salts of zinc because of exposure to artificial seawater. Thus, the surface solution of electrolyte with pH favorable for the formation of a uniform layer of these corrosion products provides a satisfactory barrier-type protective function. It can be anticipated that this effect would be cancelled in lengthy exposures to an environment with SO₂ or with SO₂ and seawater aerosol or both, and that the stabilized rate of corrosion would be the same as in the case of a parallel effect of Cl⁻ and SO_4^{2-} from the initiation of the exposure.

Technical Utilization of Results

It can be summarized that the combined effect of chlorides from seawater and SO_2 creates a more serious problem for steel as compared with zinc. The application of the results to other metals is quite impossible. It can be expected of the principles of the effects described that a deceleration of the corrosion of metals, like copper and cadmium, occurs in combined outdoor environments and that, on the contrary, the tendency of the formation of local corrosion effects should be verified by experiments with aluminum and its alloys.

The combination of both effects could be expected in actual cases and especially where products are used in industrial marine regions. Cases when metallic surfaces or surfaces with thin and damaged coats of paint will be stored or used in industrial atmospheres might occur to a small extent. According to the results of our tests, the latter case could mean an increased danger of corrosion to steel structures exported to overseas countries.

Our tests do not allow for the derivation of a suitable testing mode with a prognostic utilization. The variety of our tests has helped in the derivation of the principles of the effects, but not the kinetics controlling any individual test series. More extensive experiments with selected arrangements of tests with graduated intensity of the effect of both stimulators are therefore necessary for a detailed description of the corrosion processes. The proposal of a suitable model test could be the result.

The existing trend of the application of accelerated tests for evaluation purposes utilizes suitable combinations of exposures in standard testing equipment, that is, especially in the form of alternating exposures. It is recommended to use the cyclic testing modes (8 h: 16 h) to introduce the chlorides into the system in the form of artificial seawater and to reduce, when compared with the standard routine of tests, the deposition of chlorides to the doses approximately applied in our work unless the effect of both stimulators in the zone of the seawater spray is required.

Additional topics of importance result from the relationships chlorides and SO_2 have in the classification of the corrosivity of atmospheres and in the optimization of the corrosion protection measures in environments with a combined effect of SO_2 and seawater aerosol.

The results of the accelerated corrosion tests without the parallel test in natural environments cannot be generally applied. The knowledge that a combined environment containing both SO_2 and Cl^- causes specific effects in the initial period of corrosion rather than in steady state is considered important. It is therefore necessary to consider separate exposure periods of up to one year and the long-time exposures for which corrosion protection measures are specified.

This result suggests the desirability of an expeditious adoption of the short-time certification tests according to International Standards Organization (ISO) Corrosion of Metals and Alloys Corrosivity of Atmospheres—Method of Determination of Corrosion Rate of Standard Specimens for the Evaluation of Corrosivity (DP 9226), where the corrosivity is derived from one-year exposures of standard specimens and a comparison of these results with the estimated corrosivity from the data on environment according to ISO Corrosion of Metals and Alloys Classification of Corrosivity of Atmospheres (DP 9223), where both the simple and combined environments would be included in the system.

The guiding values of corrosion according to ISO Corrosion of Metals and Alloys Guiding Values for the Corrosivity Categories of Atmospheres (DP 9224) provide the basic engineering information for the estimation of the product life or of the protective function of a corrosion protection system. These values are derived from the corrosivity classes. The crux of the problem consists in defining a more precise classification system. The information on corrosion in combined environments can thereby supplement the data on the guiding values of corrosion.

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Degradation of Copper and Copper Alloys by Atmospheric Sulfur

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ABSTRACT: The interaction of copper and its alloys with atmospheric sulfur gases occurs in many combinations and at many rates. This paper reviews the results of experiments conducted to determine which sulfur gases cause major copper and copper alloy degradation and to study the degradation rates of copper and its alloys during exposure to the corresponding gases. Of the gases that have been studied in this work, sulfur dioxide (SO_2) , hydrogen sulfide (H_2S) , and carbonyl sulfide (COS), cause major corrosive reactions with copper and copper alloy substrates. Temperature, relative humidity, the presence of ozone, and solar irradiation have accelerating effects on the reaction rates of the gases and substrates. Copper, brass, and bronze alloys were examined. Copper generally had the highest corrosion rates. Those of the brass alloys were 50 to 100 times less than those of pure copper, and the substitution of nickel for all or part of zinc further increased the corrosion resistance of the alloy to low and moderate exposures of corrosive gases.

KEY WORDS: atmospheric corrosion, sulfur, copper, brass, bronze

The useful lifetimes of products made from metals, alloys, and other materials are often limited by atmospheric corrosion. The limitation may manifest itself in surface degradation (for example, surface film formation), deterioration of physical properties (for example, stress corrosion cracking, decreased cross section), or electrical failure (for example, circuit bridging by hygroscopic particles). To relate these phenomena to atmospheric composition, novel research apparatuses and techniques for atmospheric corrosion experiments have been developed. Five different gases were utilized in the experimental procedure to ascertain their corrosiveness. Temperature, humidity, and irradiation by simulated sunlight were also used as variables.

Experimentation

All testing was performed utilizing a computer controlled testing system [1] shown in Fig. 1. The exposure system consists of a 1-L Pyrex[®] tubular form of 8-cm-diameter with 1-cm holes randomly placed about the periphery. Sample holders are tapered plugs that are placed in the chamber holes from the outside. Samples are held on the plugs by a hook and loop fastening system and can be placed in the gas flow for a wide variety of time intervals without disturbing the gas concentrations. This is a dynamic flowing gas system with a carrier gas of air that continuously measures and records all pertinent parameters and evaluates the current system condition. If the system is not within certain preselected parametric limits, automatic adjustment is made by the computer.

Samples were cut to sizes of approximately 1 cm². Surface preparation consisted of wet sand-

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FIG. 1-Schematic diagram of the computer controlled atmospheric corrosion testing system.

ing with 600-grit aluminum oxide cloth, hand lap polishing with $1.0-\mu m$ aluminum oxide powder and a final polish with $0.3-\mu m$ aluminum oxide [2].

The gases tested in the chamber for reactivity were sulfur dioxide (SO_2) at typical concentrations in a carrier of air of 4 ppmv, hydrogen sulfide (H_2S) typically at 4 ppmv, carbonyl sulfide (COS) typically at 4 ppmv, and added ozone (O_3) typically at 0.1 ppmv. Samples were also tested for reactivity over saturated solutions of carbon disulfide (CS₂) and methyl mercaptan (CH₃SH) [3-5]. A gas was considered reactive if an exposure of 24 h to the gas produced more than 10 nm of film growth on the surface. Once a gas was established as a reactive species, further studies were performed with that particular gas by varying concentration and other parameters. Temperature of the chamber and samples were uniform and adjusted from 20 to 40°C, humidity was varied from 1 to 95% RH, and for some studies the samples were excited by simulated solar irradiation equivalent to full sunlight at ground level. For these studies a testing chamber with a quartz window was utilized [6].

Corrosion rates were calculated as nanometres of sulfide film growth per total exposure (gas concentration times hours of exposure). The actual sulfide film thickness was measured using scanning electron microscope (EDXA) techniques developed by Kammlott [7]. Kammlott's procedure is calibrated to measure the average thickness of all the sulfide species that normally form in our apparatus negating oxide measurements.

Results

Pure copper, rather than its alloys, exhibited the highest sensitivity to sulfur containing gases under virtually all conditions. H_2S and COS were found to be four orders of magnitude more corrosive than SO₂ or CS₂ [8] (Fig. 2).

Ozone and simulated sunlight had no effect on copper by themselves. However, sulfidation rates were increased at moderate to high exposures by the addition of ozone (O_3) or sunlight or both. When O_3 was added to an H_2S atmosphere, copper sulfidation rates were increased at



FIG. 2—(a) Sulfide film thickness as a function of time for different COS concentrations. All exposures were made within the experimental ranges, temperature $20^{\circ}C$ (deviation 2) and relative humidity 80% (deviation 4). (b) Sulfide film thickness as a function of total exposure to COS. The solid line is a least-squares fit to the data points. The inset compares the rate of copper corrosion by COS to that produced by H_2S exposure, as determined under the same experimental conditions.

moderate to high exposures by a factor of about three. When only sunlight was added, an increase of about a factor of two was observed. When both O_3 and sunlight were added to H_2S the sulfidation rate was increased to about that of the addition produced by O_3 alone [6] (Fig. 3).

One other atmospheric constituent was tested, methyl mercaptan (CH_3SH), and was not found to cause appreciable reactions with copper or any of its tested alloys.

We have looked at both pure and alloyed metals. Nickel and zinc are quite sulfidation resistant, while copper sulfidizes readily (Fig. 4) [9,10]. The addition of nickel to pure copper decreases sulfidation at a rate exponentially dependent on the amount of alloying nickel (Fig. 5). Thus, 92 copper/4 nickel/4 tin sulfidizes much less rapidly than pure copper, and increasing the nickel content to 9 wt% lowers the rate such that less than 10 nm of sulfide film may be expected in a typical field environment only over a decade of exposure to the environments tested.



FIG. 3—Average thickness of the cuprous sulfide corrosion film as a function of H_2S exposure (the product of H_2S concentration and exposure time); (a) exposure to H_2S (2.3 ppm) and O_3 (0.17 ppm); (b) exposure to H_2S (2.3 ppm) and light; (c) exposure to H_2S (2.1 ppm), O_3 (0.20 ppm), and light; (d) fitted curves from (a) to (c). The solid lines and squares are for exposures to H_2S in the absence of both O_3 and incident radiation; the circles and broken lines are for exposures to H_2S in the presence of either O_3 or incident radiation or both. For all experiments the temperature was $21^{\circ}C$ (deviation 0.5) and the dew point was $19.9^{\circ}C$ (deviation 0.6). The precision of each measurement is a negligibly small fraction of its range.

To investigate the relative merits of nickel and tin as sulfidizing inhibitors, alloys having similar concentrations of one metal and dissimilar concentrations of the other were exposed to corrosive environments. At 9 wt% nickel, the removal of 4 wt% tin (from 6 to 2) had little effect on sulfidation. At 4 to 5 wt% tin, the removal of 4-wt% nickel (from 4 to 0) resulted in a sulfidation rate similar to that for pure copper. This is consistent with an interpretation that sulfidation is inversely related to nickel content [3], a result supported by corrosion studies of bronzes (copper-tin alloys not containing nickel) (Fig. 6).

Comparative sulfidation tests of an 85 Cu/9 Ni/6 tin alloy prior to and subsequent to spinodal heat treatment demonstrated that the spinodal structure tended to sulfidize more rapidly, although the rate was still moderate [11] (Fig. 7). This result must be related to the structure of the spinodal alloy, but the exact mechanism remains uncertain.

Comparative sulfidation tests of the 72500 alloy (89 Cu/9 Ni/2 Sn) in annealed and work



FIG. 4—Cu₂S film thickness as a function of total exposure to H_2S . The 46400 alloy is 40% zinc, 60% copper; the 71500 alloy is 30% nickel, 70% copper; the 75200 alloy is 17% zinc, 18% nickel, and 65% copper. The upper line is from 10200 (99.95 oxygen free copper).



FIG. 5—Film thickness () as a function of weight percent nickel for 2.5 ppm/h of H_2S exposure.

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FIG. 6—Histogram of various ternary Cu-Ni-Zn combinations shown at incremental sulfiding exposures along with their corresponding sulfide formation thicknesses.



FIG. 7—Film thickness as a function of total exposure for the 72700 alloy (85 Cu/ 9 Ni/ 6 Sn) prior to and following heat-treatment to produce spinodal structure.

hardened states demonstrated that the latter was the more resistant to sulfidation (Fig. 8). This result is consistent with work by others on copper-nickel binary alloys, but is in contrast with the conventional picture that the cold working of materials increases their tendency to corrode. More extensive experiments will be needed to explore in detail the relationship between corrosion and cold-working of copper alloys [11].

Conclusions

Of the gases that were studied, SO_2 , H_2S , and COS cause major corrosive reactions with copper and copper alloy substrates. Temperature, relative humidity, the presence of ozone, and solar irradiation had accelerating effects on the reaction rates of the substrates and gases.

Of the metals that were studied, copper generally had the highest corrosion rates. Those of the brass alloys were 50 to 100 times less than that of pure copper and the substitution of nickel for all or part of zinc further increased the corrosion resistance of the alloy to low and moderate exposures of corrosive gases.



FIG. 8—Film thickness as a function of total exposure for annealed (solid line) and work hardened (dashed line) samples of 72500 alloy (89 Cu/9 Ni/2 Sn).

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DISCUSSION

Robert Baboian¹ (written discussion)—Do you feel that a test duration of less than 100 h can adequately represent the behavior of metals in the atmosphere where 10 years is sometimes considered a normal exposure period?

John Franey (author's closure)—The work described in this paper is not intended to reproduce the complex interactions of hundreds of atmospheric species with copper and its alloys. As the title suggests, the work involves only sulfurous gas interactions. The intent in this work is to deal with specific processes involved in atmospheric corrosion. The research should thus be regarded as among the few with the aim of achieving a detailed understanding of a limited but important part of the process. Only when enough of these studies are completed can one predict what interactions will occur on a substrate placed outdoors for a "normal ten-year exposure."

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Marine Salts Contribution to Atmospheric Corrosion

REFERENCE: Duncan, J. R. and Ballance, J. A., "Marine Salts Contribution to Atmospheric Corrosion," *Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society of Testing and Materials, Philadelphia, 1988, pp. 316-326.*

ABSTRACT: The effects on atmospheric corrosivity of carriage of sea-salt inland from ocean coasts have been largely neglected by researchers except for regions within a few kilometers from the sea. In island nations, salt-affected zones can cover large percentages of total land area. The extent of carriage of sea-salt inland, and correlation to this of the corrosion rates of metals, is assessed in two areas of New Zealand. A sheltered surface collector is erected at each of 18 sites at up to 90 km inland. The site had been chosen to minimize the likelihood of industrial pollution. Each collection rack had attached to its top a test unit with an aluminum wire on a threaded stud (Climat test unit) and a rod holding a pair of steel coupons. There was very good correlation of the steel corrosion rate (48 weeks of exposure) to the log (chloride deposition), and to the 48-week average steel stud value in the 12-week Climat test. The Climat test, because of its ease of performance, thus seems to be a cost-effective means of assessing likely corrosion rates at distances 20 km and more inland are higher than might have been expected from published reports of studies on continental land masses.

KEY WORDS: aluminum, atmosphere, chlorides, corrosion, measuring, New Zealand, sea-salt, steel

The carriage of sea-salt inland from coasts has long been recognized as an important contributor to atmospheric corrosion problems in most maritime regions. The most thorough study of this subject reported is that by Ambler and Bain in Nigeria [1], though many textbooks and authors have based their statements on an earlier report [2] of a smaller set of values found in Nigeria. These studies found chloride deposition decreases with distance inland, with a consequent decrease in atmospheric corrosion. Most of the decreases occurred within a kilometer or two of the shore. But the authors seem to have mainly confined themselves to discussing this rapid decrease in corrosivity close to the shore, rather than looking deeply into the effects of seasalt further inland. The rapid decrease is important in assessing the corrosivity variations to be expected at exposure sites within this distance of the shore if the comparability of results at different sites is to be understood. However, it has much less relevance to the precautions that must be taken in the design of a structure at a distance of, say, 20 km inland. The designer recognizes that if his structure is immediately adjacent to a beach, he will need to take special precautions, but he has much less guidance on how to assess his problems further inland.

Over 1984 to 1985, corrosion tests and measurements of the levels of chloride deposited by wind onto sheltered surfaces were performed at 18 sites at up to 90 km from the sea in two regions of New Zealand [3]. This work was undertaken because there seemed to be unexpectedly high atmospheric corrosion rates inland along the path of prevailing winds blowing from the

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sea. A characteristic of the climate of these regions is long periods of relative humidity exceeding 80%. Since sodium chloride can take up water from the atmosphere at these humidities, sea-salt deposits (especially on surfaces that are sheltered from rain) can pose severe durability hazards to metal building claddings.

Neutron activation analyses of the chloride collection surfaces showed that even 50 km inland, the ratio of sodium to chloride was still approximately correct for the chloride to have been of marine origin [3]. This paper discusses the correlations between amounts of chloride deposited and the corrosion measurements found in this recent study, and compares the relationship of corrosion rate to distance from the sea with that suggested by Ambler and Bain and other workers.

Experimental Procedure

Selection of Monitoring Sites

Monitoring sites for the study were in an approximate geometric progression of distance inland from coasts that had prevailing winds blowing off the sea onto the land, across fairly flat countryside at least for the first 30 km. The availability of reliable meteorological data was also taken into account. (It was hoped that wind run and gust data could be used as variables in the analysis of the results, but this proved impossible because there were insufficient sites with these data.) Sites were initially selected to try to avoid industrial pollution sources, which could be expected to interfere with the experiment. The locations are listed in Table 1.

		Chloride I Rate,		
Site	Distance from Coast, km	Mean	Maximum	Rain in Test Period, mm ⁴
Manawatu				
Tangimoana	0.8	21.9	53.8	NR
Paraparaumu	1	11.3	25.1	913
Flockhouse	4.5	6.4	15.0	915
Clydesdale	7	6.0	16.3	NR
Levin	8	2.6	8.9	1007
Bulls	13.5	1.7	4.5	NR
Kairanga	20.5	4.0	8.2	725
Palmerston North	33	2.3	6.0	807
Ballantrae	52	3.1	6.3	NR
Southland				
Oreti Beach	0.6	34.1	108.6	NR
Tiwai Point [*]	5.5	28.5	64.3	808
Clifton	8	12.9	23.4	NR
Invercargill Aero	8.5	7.8	14.9	914
Myross Bush	16.5	2.4	6.0	NR
Woodlands	28	0.5	0.9	927
Brydone	49	2.2	3.9	NR
Gore	64	1.0	2.0	782
Tapanui	94.5	0.4	0.8	773

TABLE 1-Site locations and 28-day chloride dry deposition rate and rainfall data.

"Rainfall data collected by NZ Meteorological Service station. NR = not recorded at this site. ^bOn sandy harbour beach, 5.5 km from nearest ocean shore.

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Collection of Dry-Deposited Chloride

The collector used is described by Cawse [4]. A horizontal sheet of filter paper (Whatman 541, 200×250 mm) supported on a perspex sheet of approximately the same size is mounted centrally beneath a one-m square perspex cover supported at each corner (to shield the paper from rain). This filter paper surface is approximately 1350 mm above the ground. The paper surface is collected and renewed each 28 days. On recovery, the chloride is extracted from the paper using a Soxhlet apparatus by refluxing with deionised water. The chloride concentration is determined in the resulting solution using a chloride-specific electrode. Control samples that were never exposed are put through the analysis procedure at intervals.

Corrosion Rate Determinations on Steel Panels

Projecting from the top of each chloride collection rack is a bracket with two steel coupons attached, with an insulated bolt through the centre of each coupon so that the coupons are held vertically, approximately 120 mm from the bracket. The coupons were produced from steel cast by BHP Research Laboratories in Australia to an alloy composition (Table 2) which corrodes at a rate relatively insensitive to minor variations in composition [5]. The steel was hot and cold rolled to 3.2 mm strip, which was then guillotined to 100×50 mm coupons. These were annealed and drilled with an identification pattern of four 1.59 mm holes at one edge of each coupon before supply to the Building Research Association of New Zealand (BRANZ).

Before exposure, the coupons are lightly rubbed with steel wool, degreased, then immersed in 5% hydrochloric acid solution at 80° C for ten min. They are then rinsed in cold running tap water for ten min, immersed in boiling water, and air dried. Each is weighed to 0.1 mg and stored in a dessicator until ready for exposure. The exposure period is 48 weeks. Upon retrieval, the coupons are immersed in a solution of 50 g stannous chloride per litre of concentrated hydrochloric acid to remove corrosion products, and rinsed thoroughly. The coupons are reweighed to 0.1 mg and the corrosion rate calculated as a function of the total exposed area of the coupon. (This follows the procedure adopted by King et al. [5].)

Galvanic Corrosion Evaluation of Aluminum

A Climat test unit [6] is attached to the top of each chloride collection rack. This comprises aluminum wire wrapped around 1.27 mm (0.5 in.) BSW threaded studs made of mild steel, copper and nylon, respectively, which are screwed into a solid base. The wire used is Alloy 1350 [7], 0.9-mm diameter hard-drawn, supplied by Alcan (NZ) Ltd.

Before assembly, the components are cleaned in petroleum ether, air dried, then rinsed in acetone and again air dried. The wire (approximately 900 mm long) was weighed to 0.1 mg, wound tightly around the stud, and held in place by short lengths of insulated wire. The exposure period was 84 days (to correspond to a multiple of 28 day periods of chloride collection). Upon retrieval, the wire is removed from the stud and immersed in a boiling solution of 20 g/L chromic acid, 40 g/L phosphoric acid for 10 min to remove the corrosion products. After rinsing in hot water, then acetone, the wire is reweighed to 0.1 mg and the percentage weight loss calculated. Unpublished studies at BRANZ have shown this method (modelled on that used by Doyle and Godard [8]) produces negligible weight losses on control samples.

с	Mn	Si	Р	S	Ni	Cr	Cu
0.16	0.61	0.05	0.01	0.026	0.27	0,12	0.22

TABLE 2—Composition of steel panels.

Results

The amount of chloride deposited onto the collectors differs widely from month to month. The mean and maximum 28-day chloride deposition rates at each site over the 48-week period of the study are listed in Table 1. The steel coupon corrosion rate and the mean aluminum wire percentage weight losses from the Climat units at each site are listed in Table 3. The steel coupon rates are the average from the two coupons at each site. The Climat values are the average for the single units at each site over the four test periods. Typical data are given in Table 4.

Figures 1 to 8 show some of the relationships found between the amounts of chloride deposited, the 84-day Climat tests, and the 48-week steel corrosion rates. Table 5 lists the correlation details for the complete data sets for chloride deposition, the 84-day mild steel stud Climat tests, and the 48-week steel corrosion rates. The steel stud results were chosen for use in this further development because this stud has been described as that most affected by a marine environment [6].

Discussion

A very good correlation has emerged between the values found on the mild steel stud in the Climat test and the corrosion rates of the steel coupons. There has also been good correlation of the corrosion measurements using the mild steel stud in the Climat test to the logarithm of the deposited chloride, and very good correlation of the steel coupon corrosion rate to the logarithm of the deposited chloride.

These correlations are important in assessing the validity of using the Climat test in selecting materials or methods of protection against atmospheric corrosion. The Climat test is relatively cheap and simple to perform, and particularly so as compared with the analysis for chloride deposition, whether using the wet candle technique of Ambler and Bain or that used in the present study. There is very large variability from month to month in the dry deposition of

	Ave Re	Average Climat Test Results. %wt Loss				
Site	Mild Steel	Copper	Nylon	Corrosion Rate for Steel, μm/year		
Manawatu						
Tangimoana	12.25	14.37	0.24	39.2		
Paraparaumu	9.36	10.22	0.24	36.4		
Flockhouse	8.62	8.52	0.14	31.6		
Clydesdale	8.01	8.01	0.20	33.5		
Levin	5.67	5.33	0.08	18.9		
Bulls	5.46	5.67	0.14	22.6		
Kairanga	6.76	5.72	0.15	26.4		
Palmerston North	5.20	4.85	0.10	25.2		
Ballantrae	5.50	5.17	0.10	25.3		
Southland						
Oreti Beach	12.76	16.23	0.21	41.2		
Tiwai Point	11.83	11.80	0.27	40.9		
Clifton	10.32	12.32	0.20	37.8		
Invercargill Aero	8.68	8.30	0.15	32.8		
Myross Bush	5.77	5.55	0.09	20.9		
Woodlands	2.97	3.40	0.08	12.2		
Brydone	5.68	5.93	0.11	22.1		
Gore	3.31	3.82	0.07	13.8		
Tapanui	1.48	1.82	0.06	7.0		

TABLE 3—Results of corrosion tests done at collection sites.

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	Test Period 1984-5						
Site	May to Aug.	Aug. to Oct.	Oct. to Jan.	Jan. to Apr.			
- Tiwai Point							
Climat units							
Mild steel	17.32	10.08	10.53	9.38			
Copper	17.42	10.98	9.72	9.06			
Nylon	0.33	0.26	0.34	0.14			
rainfall, mm	158	216	194	241			
Invercargill Aero							
Climat units							
Mild steel	9.78	8.23	8.95	7.75			
Copper	9.36	9.08	8.02	7.94			
Nylon	0.16	0.24	0.15	0.06			
rainfall, mm	186	229	215	283			
Gore							
Climat units							
Mild steel	4.54	3.20	2.90	2.58			
Copper	4.94	4.01	2.90	3.42			
Nylon	0.13	0.11	0.05	0.00			
rainfall, mm	147	221	195	219			

 TABLE 4—Actual Climat values recorded for three sites in Southland, and rainfall data for the test periods.



FIG. 1—Relationship of steel corrosion rate (μm /year) to the 48-week total chloride deposition on the sheltered collector ($\mu g/cm^2$).



FIG. 2—Relationship of steel corrosion rate ($\mu m/year$) to the logarithm of the 48-week total chloride deposition on the sheltered collector ($\mu g/cm^2$).



FIG. 3—Relationship of steel corrosion rate ($\mu m/year$) to the logarithm of the first four weeks chloride deposition on the sheltered collector ($\mu g/cm^2$).



FIG. 4—Relationship of steel corrosion rate ($\mu m/year$) to the percentage weight loss from the aluminum wire on the steel stud in the Climat test over the first twelve weeks.



FIG. 5—Relationship of steel corrosion rate ($\mu m/year$) to the average percentage weight loss from the aluminum wire on the steel stud in the Climat test over the four 12-week periods.



FIG. 6—Relationship of the percentage weight loss from the aluminum wire on the steel stud in the Climat test to the logarithm of the first four weeks chloride deposition on the sheltered collector ($\mu g/cm^2$).



FIG. 7—Relationship of the percentage weight loss from the aluminum wire on the steel stud in the Climat test to the logarithm of the total twelve weeks chloride deposition on the sheltered collector $(\mu g/cm^2)$.



FIG. 8—Relationship of the percentage weight loss from the aluminum wire on the nylon stud in the Climat test to the logarithm of the total twelve weeks chloride deposition on the sheltered collector ($\mu g/cm^2$).

chloride, as shown in Table 1. It would be unwise to categorize the possible corrosivity of a site on the basis of a single month's chloride deposition measurement. There is also the possibility on sheltered surfaces that will not be washed by rain that a single storm could deposit sufficient chloride to pose major corrosion hazards to these surfaces even in a less generally corrosive zone. Since this test has been done at many sites around the world (see, for example, the lists by Doyle and Wright [6]), it offers the possibility that a new site could be put into a wider context, and allows past experience at other sites to be used as a guide to the corrosion problems to be anticipated, provided it has a basic validity. This study, performed in two widely separated regions in New Zealand, suggests that the Climat test does have a basic validity, at least for sites which can be categorized as dominantly affected by sea-salt deposition. The variability from season to season of values in the Climat test (Table 4) has been observed by other workers also [6]. From the data in Table 4, it is obviously not related simply to rainfall in the present study. It probably is related to wind blowing from the sea, but this could not be proven conclusively from the weather data available.

The qualification regarding the dominant effects of sea-salt should be emphasized. The success of the correlation in this instance is possibly enhanced by the choice of monitoring sites, which were expected to be free of significant industrial pollution. Thus, for example, Ambler [9] found a similar drop in chloride concentration with increasing distance inland in United Kingdom as compared to that found in Nigeria, but did not find such a clear relationship between distance and corrosion rate as had been found in Nigeria. He attributed this difference to the effect of industrial pollution. Hayward (personal communication) had described how to

TABLE 5—Correlation equations and coefficients.

FIG. 2 Steel Coupon Corrosion Rate = -19.7 + 7.88 ln (total of twelve 4-week chloride deposition rates) Correlation Coefficient: r-squared is 95.1% FIG. 3 Steel Coupon Corrosion Rate = -2.66 + 8.27 ln (chloride deposition rate in first 4 weeks) Correlation Coefficient: r-squared is 93.5% FIG. 4 Steel Coupon Corrosion Rate = 5.61 + 2.59 (first steel-stud Climat value) Correlation Coefficient: r-squared is 88.9% FIG. 5 Steel Coupon Corrosion Rate = 5.23 + 0.832 (sum of four steel-stud Climat values) Correlation Coefficient: r-squared is 93.6% FIG. 6

Steel-Stud Climat Value = -1.17 + 2.11 ln (chloride deposition rate in first 4 weeks) Correlation Coefficient: r-squared is 72.0%

FIG. 7

Steel-Stud Climat Value = $-3.94 + 2.33 \ln$ (total of three 4-week chloride deposition rates) Correlation Coefficient: r-squared is 80.6%

Fig. 8

Nylon-Stud Climat Value = -0.0354 + 0.0372 ln (total of three 4-week chloride deposition rates) Correlation Coefficient: r-squared is 33.6%

NOTE: Steel coupon corrosion rate is in μ m/year; chloride deposition is in μ g/cm²; Climat value is in percent.

correct the value for the A1/Cu stud, for the marine influence, so that it can be used to assess industrially generated atmospheric corrosivity, using the expression:

(Industrial Corrosion Index) = (A1/Cu Value) - 1.22(A1/Mild Steel Value)(1)

Values below 0.5 are negligible. When this is done, only the Oreti Beach site in each of the first three periods gives significant values. The reason for this is not understood, since the collector was sited more remotely from roads, etc., than most of the other collectors.

It is interesting to observe the good correlation of the 48-week steel corrosion rate to the first four-week chloride deposition, which might be taken to confirm the warning of others [10] that the initial exposure conditions have a very important effect on the subsequent corrosion. However, there is also very good correlation of this corrosion rate to the total chloride deposited over the whole 48 weeks, and the four-week result may simply indicate that the initial four weeks were fairly typical of the whole year.

Atmospheric corrosion rates on fully rain-washed nonferrous metal surfaces in New Zealand are generally low compared to some other countries [11]. Though no nonferrous metal panels are used in the present study to assess the correlation of their corrosion rates to the chloride deposition rates, this general trend of low nonferrous metal corrosion rates is reflected by the fairly low values for the nylon stud when compared to some of the values listed by Doyle and Wright [6]. It will be noted from Fig. 8 that the correlation of values found for this stud to the

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deposited chloride is fairly poor, and this is presumably because the rainfall (see Table 1) has regularly washed away the deposited chloride. In instances where metal roof claddings in eaves become perforated by corrosion in New Zealand, the corrosion is very frequently from the underside, reflecting this benefit from rainwashing. The atmospheric corrosion mechanism of mild steel differs from that of nonferrous metals in that on steel, the chloride aggregates at the metal/rust interface, while on the others, it is at the corrosion product/atmosphere interface [12]. Because of this difference in mechanisms, removal of chloride by rainwashing is much more difficult from corroding steel surfaces. In the present study, there was fairly comparable rainfall at all sites within each region over the course of the exposure test (Table 1), so that differences in rainfall have not been a significant contributor to the differences in corrosion rate. Presumably, this regular rainfall, which is an advantage in washing the surfaces of the nonferrous metals, has had the effect, in the present study, of simply increasing the time-of-wetness, and hence the corrosion, of steel. (Rainfall in New Zealand also contains a lot of dissolved chloride [11]. It might, therefore, be expected that a low residual level of chloride is left on the surface, even after rain.)

There have been very few reports of direct comparisons made between corrosion rate and chloride deposition. It has been customary, on the basis of the studies in Nigeria [1,2], to expect that the chloride concentration drops off rapidly with distance from the coast, and with it the corrosivity of the natural atmosphere. This view has probably been strengthened in European minds by the production of a report for the Commission of European Communities [13], which shows reduction to very low background levels within 5 km of the sea for many sites as part of an assessment of exposure test site severity. These "continental" measurements are, however, almost certainly not transferable to oceanic sites. In a paper which seems to have been largely ignored by corrosion scientists, Brierly [14] collated available data on total chloride precipitation at sites around the world and proposed four "atmosphere seasalts design criteria areas," into which he categorized all land masses. Brierly emphasized the importance of geography in determining the amount of seasalt deposited; thus, because the wind is predominantly westerly across Scandinavia, values of 12 kg/ha/year were found for chloride deposition in Norway, but only a few per cent of this on the eastern coast of Sweden. This is reflected in the greater corrosiveness of the atmosphere in Norway [15]. Oceanic islands, especially if they lie in strong wind flows that travel extensive distances across the sea, fall in Brierly's most severe zone, and the direction and strength of the wind is more important than the distance inland in determining the saltfall. Thus New Zealand, a chain of islands in a latitude belt of strong winds, might be expected to show rather different effects from Nigeria or Europe in the relationship of seasalt deposition to distance inland.

This geographic effect on atmospheric corrosivity zones on small islands has been reported previously for Cuba [16], where the chloride in the atmosphere was determined to be the major corrosive influence, and for Barbados [6]. The latter workers proposed a relationship between the cube roots of the corrosion rate (or the atmospheric salinity) and the distance inland, which they said fitted to the Ambler and Bain data from Nigeria and to data collected in the Republic of South Africa for distances up to 16 km inland. It is not clear from their paper whether it fitted to their data from Barbados. Application of this relationship to their data from South Africa and to the data from the two regions of New Zealand examined here is shown in Figure 9. The relationship appears to be of doubtful validity for the South Africa data, and to be invalid for the New Zealand data. The decrease in corrosion rate with distance inland is too slow.

Conclusions

For an environment that can be expected to be fairly free of industrial pollution, the Climat test is well-correlated to steel corrosion rates and to the amount of chloride deposited onto sheltered surfaces. Because it is a relatively simple test to perform, this test is a cost-effective means of assessing the dangers of atmospheric corrosion in such environments. The extent of chloride



FIG. 9—Test of cube root relationship of the type (distance from sea (km))^{1/3} + (average Climat value, mild steel stud)^{1/3} = const proposed by Doyle and Wright [6].

carriage inland, and hence the hazard of atmospheric corrosion, is higher on oceanic islands than might be predicted from the classic studies of corrosion versus atmospheric salinity made in Nigeria, or from the extensive studies made in Europe. The geography has a very important influence. This must be taken into account in specifying corrosion protection measures for structures in these environments.

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DISCUSSION

R. Baboian¹ (discussion questions)—Our work at Texas Instruments has shown that a correlation of chloride composition with corrosivity in the atmosphere is complicated by the presence of acid deposition. In the combination of acid deposition and chloride salts, HCl is formed which vaporizes off during dryoff periods. Subsequent analysis of the corroding system for chloride composition gives misleading results because of this behavior.

J. Duncan (author's closure)—We could believe that such volatilisation does occur. However, we are reasonably confident that the measurements of chloride deposition in this study were not affected by this factor because the collection sites were chosen to be away from likely sources of industrial pollution. We have not attempted to measure concentrations of chloride upon the actual corroded samples.

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The Chemistry of Precipitation: Perspectives on Potential Impacts on the Corrosion of Metals

REFERENCE: Graedel, T. E., **"The Chemistry of Precipitation: Perspectives on Potential Impacts on the Corrosion of Metals,"** *The Degradation of Metals in the Atmosphere, ASTM STP* **965. S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 327-335.**

ABSTRACT: The corrosion effects of acid deposition can be assessed properly only if the frequencies of occurrence of different forms of precipitation are specified and if the chemical constituents and reactions in precipitation are understood. Knowledge of precipitation chemistry is increasing at a rapid rate, and it is therefore useful to summarize the present understanding about the corrosive constituents that occur in precipitation, their typical concentrations, their temporal variability, and their probable long-term trends. Such information is given in this paper for acidity, sulfate, nitrate, chloride, ammonium, and organic acids in rain, fog, and dew.

KEY WORDS: precipitation, atmospheric corrosion, metals

Nearly all atmospheric corrosion involves liquid water. This water can be condensed from the atmosphere onto surfaces if relative humidities are high and surface temperatures are low (the formation of dew), but water is also supplied by active precipitation (rain, snow, or fog). Atmospheric water is not pure, as is well known, but is a complex chemical solution containing a number of reactive molecules, radicals, and ions. Much of the degradation of metals that occurs upon exposure to the atmosphere is a consequence of the interaction of the metals with these trace species in precipitation. To assess the potential degradation of a metal upon atmospheric exposure, therefore, it is necessary to specify three factors: the frequency of precipitation, the chemical constituents of that precipitation, and the susceptibility of the metal to those constituents.

The goal of the present work is to provide a perspective on the three factors mentioned above. The presentation begins by reviewing the moisture deposition and duration of different types of precipitation. Information on temporal variability is then provided, since different locations can be significantly different in this regard, with consequent effects on metals degradation. Next, a summary of the chemical constituents of precipitation is given. As with the frequency of occurrence, the chemistry of precipitation can show substantial variation; a few examples of this type of behavior are presented. Information is then given on long-term trends of some atmospheric constituents of interest. Finally, the susceptibility of metals to atmospheric corrodents is briefly summarized.

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Precipitation Occurrence

The variability of the occurrence of precipitation throughout the world is great, and differences in the corrosion potential of different locations have been studied for many years. To provide some idea of the magnitude observed, it is of interest to show some typical values and extremes for atmospheric phenomena. In Table 1, such information is presented for dew, fog, rain, and snow [1]. Several features of this table deserve comment. The first is that dew and fog have similar typical moisture deposition values. Dew occurs much more often, however, with each occurrence depositing much less moisture than is deposited during fog.

For rain and snow, similar wide ranges are present in moisture deposition at different locations. The typical values of moisture deposition are similar for the two forms of precipitation, as are their annual durations. Thus, in the midlatitudes with typical precipitation patterns, rain and snow dominate the amount of moisture deposited on exposed surfaces, but the duration of exposure to dew is the longest of any of the precipitation types.

Duration of Individual Precipitation Events

Precipitation events themselves are of greatly differing length and intensity. A nice demonstration of the variation in rainfall is presented by Evans et al. [2] for several stations within the continental United States. Figure 1, reproduced from that study, shows the variation in rain

	Annual Moistur	e Deposition, mm	Annuai I	Annual Duration, h		
Phenomenon	Range	Typical Value	Range	Typical Value		
Dew	0 to 100	30	0 to 1500	750		
Fog	0 to 40	25	0 to 150	60		
Rain	30 to 6500	700	10 to 3000	300		
Snow	0 to 9000	750	0 to 3000	300		

 TABLE 1—Occurrence of atmospheric phenomena at mid-latitude

 North American sites.



FIG. 1—Frequency distribution of ambient rainfall shower durations from the period of 30 May through 29 September, 1981 at Brookhaven National Laboratory, Upton, Long Island. New York. A shower is defined as a precipitation event in which no additional precipitation occurs within 60 min after the end of the event. Other rainfall shower durations of 215, 240, 263, 307, 320, 366, 367, 434, 482, 932, and 1975 min were not plotted. These higher-duration rainfalls accounted for 11.0% of all showers. During the growing season there were 48 other showers with a duration of less than one minute with less than 0.25 mm of rainfall per shower. These showers are not included in this figure. (Reproduced with permission from Ref 2.)

shower duration during the summer at a site on the U.S. Atlantic Coast. Most rain lasts less than an hour. The precipitation amounts produced by the showers are shown in Fig. 2. The vast majority of events produced less than 0.3 mm of rainfall. The authors summarize the results by saying that surfaces exposed to rainfalls will be wetted by numerous showers of short duration and low volume.

The duration of dew events is as illustrated in Table 2 for six years of measurements in April, May, and June in Pendleton, OR, one of the very few locations for which data on dew are available. Dew events tend to be quite long (five h or more). The occurrence of dew is strongly dependent on high relative humidity, with nearly all days on which dew formed having relative humidity >90% lasting for eight h or more.

Other forms of precipitation also show large differences among individual events. Fogs may be of short duration or many hours long, as is the case for snowfalls. In all cases where corrosion



FIG. 2—Frequency distribution of ambient rainfall shower depths from the period of 30 May through 29 September. 1981 at Brookhaven National Laboratory. Upton, Long Island. New York. A shower is defined as a precipitation event in which no additional precipitation occurs within 60 min after the end of the event. Other rainfall shower amounts of 12.7, 16.0, 22.9, 32.4, and 43.0 mm were not plotted. These higher rainfalls accounted for 5.0% of all showers. During the growing season there were 48 other showers with a duration of less than one min with less than 0.25 mm of rainfall per shower. These showers are not included in this figure. (Reproduced with permission from Ref 2.)

Dew Duration, h	Number of Days	Average Duration of $\geq 90\%$ Relative Humidity, h
0	158	4.77
1 to 4	28	9.29
5 to 8	52	8.54
9+	86	11.31

TABLE 2—Average duration of relative humidity \geq 90% for selected intervals of dew duration at the Pendleton Experimental Station.^a

"From Ref 3.

processes occur rapidly, it is therefore necessary to study individual precipitation events rather than ensemble averages.

Chemical Constituents of Precipitation

Precipitation contains inorganic and organic ions, radicals, and molecules, often in surprisingly large concentrations. In Table 3, typical values of the major trace species for rain, fog, and dew in various U.S. locations are presented. (Limited measurements of snow chemistry suggest that it is similar to rain.) Among the points worth noting are that fog tends to be much more acid than rain, and dew somewhat less so. Fog drops are smaller than rain drops, and their higher acidity has been attributed to lower dilution of ionic species from scavenged aerosol particles. For similar reasons, concentrations of other inorganic ions are much higher in fog as well. The ammonium ion, the only base available to buffer the acidic components, is extremely concentrated in fog. In the case of dew, basic soil particles present on surfaces prior to dew formation are thought to limit the acidity. Another interesting feature of Table 3 is the relatively high levels of organic acid anions in rain. These species are presumably high in other forms of precipitation as well, but measurements remain to be made. The organic acids contribute to the total acidity of the precipitation, and are themselves corrosive to metals [4]. Also present at relatively high concentrations is hydrogen peroxide, a powerful oxidizer thought to promote acid formation from precursor atmospheric gases.

Temporal Chemical Variability

The concentrations of chemical species shown in Table 3 are typical of results from precipitation collected throughout an entire event. If the precipitation chemistry is examined with greater time resolution, it is seen that substantial variations occur within an event. Such a pattern is illustrated in Fig. 3, which shows hydrogen ion, sulfate ion, and nitrate ion concentrations as measured during a typical rainfall. As can be seen, a rapid decrease in sulfate ion (SO_4^{2-}) and ammonium ion (NO_3^{-}) occurred during the initial portion of the rainfall, while the H⁺ concentrations were variable. This behavior is attributed to temporally heterogeneous scavenging by acidified rain of soil dust with acid neutralizing capacity, since soil cations often follow the concentration patterns of the anions of Fig. 3. Similar temporal behavior for concen-

Species	Fog [*]	Rain ^c	Dew ^d			
H+	100 to 5600	10 to 100	0.5 to 315			
pH	2.2 to 4.0	4.0 to 5.0	3.5 to 6.3			
NH ⁺	370 to 10500	0.1 to 39	1 to 65			
CI-7	56 to 1100	0.5 to 1800	0.3 to 105			
NO ₃	130 to 12000	0.3 to 50	3 to 190			
SO ₄ ²⁻	62 to 5060	1 to 150	10 to 250			
HCO7		4 to 36				
CH ₃ CO ₂		1 to 10				
(COO) ₂		33				
H ₂ O ₂		10 to 70	• • •			

 TABLE 3—Typical concentrations^a of reactive constituents in precipitation.

"Microequivalents per liter, except for H_2O_2 (micromoles per liter) and pH.

^bRef 11 and 12.

^cRef 13. except Ref 14 { $(COO)_2^{2-}$ } and Ref 15 { H_2O_2 }. ^dRef 16 and 17.



FIG. 3—Concentrations of H^+ , SO_2^{2-} and NO_3^- in sequential samples of rain collected at Holland, Michigan on June 19, 1980. (Reproduced with permission from Ref 5.)

trations in rain is common as well for soluble gases such as hydrogen peroxide (H_2O_2) [6]. Where windblown soil aerosol is less abundant, rain acidity generally decreases throughout a rain event [7].

Complex chemical behavior is also displayed by fog. In Fig. 4, data from fog studies in the Los Angeles Basin are reproduced [8]. The data require both meteorology and chemistry for interpretation, since they concern a fog that maintained itself in the presence of reversing sealand air flows. The high ionic concentrations early in the event are attributed to the incorporation of particles with high ionic loading from Los Angeles. Later in the event, the concentrations decrease due to two factors: the dilution of the droplets as additional water is accreted onto them and the influx of cleaner air from the ocean. In contrast, events in which the air mass is stable show the highest ionic concentrations at the end of the fog event, as the water in the droplets begins to evaporate and the solutions become increasingly concentrated [8].

Concentration Trends of Corrosive Atmospheric Species

Previous sections of this paper have demonstrated variations in the frequency of occurrence, duration, and moisture deposition of precipitation, and in the concentrations of corrodents in different precipitation events and within the same event. Longer-term effects are also present in the corrodent concentrations as a result of changes in the emission fluxes of the corrodent precursors. In Fig. 5, the long-term trend of sulfur dioxide in U.S. urban atmospheres is illustrated using the box-plot technique diagrammed in Fig. 6. The sources of emissions of sulfur dioxide, the precursor to sulfuric acid and the sulfate ion in precipitation, are dominated by fuel combustion. As increased controls and cleaner fuels have been used over the past decade, sulfur dioxide (SO_2) medians and composite averages have steadily decreased. It is anticipated that this trend will continue.

Nitrogen dioxide (NO_2) is the precursor of the nitrate ion found ubiquitously in precipitation. NO₂ emission fluxes are divided roughly equally in the United States between motor vehicles and stationary combustion sources. The emissions increased slightly in the late 1970s, de-



FIG. 4—Fogwater ion concentrations at Del Mar, CA on Jan. 8, 1983. pH values are indicated on top of each data bar. (Reproduced with permission from Ref 8.)



FIG. 5—Box-plot comparisons of trends in annual mean sulfur dioxide concentrations at 286 United States sites. 1975 to 1983. Most of these sites are in urban areas. NAAQS indicates the U.S. national ambient air quality standard for SO₂. (Reproduced from Ref 10.)



FIG. 6—The plotting convention used in Fig. 5 and 7 of this paper. (Reproduced from Ref 10.)

creased slightly in the early 1980s, and are now relatively stable. This emission pattern is reflected in atmospheric concentrations, as seen in Fig. 7. Major changes in the concentrations of nitrogen dioxide are not anticipated over the next few years.

Trend information on other corrosive atmospheric species is much sparser and less satisfactory. In the case of ammonia, the sources appear to be bacterially related, with sewage treatment plants, fertilizer, marshes, and similar environments as major contributors. Some of these sources may show slight decreases over the years, but the ammonia cycle is sufficiently uncertain that no firm prediction for long-term atmospheric ammonia concentrations can be made. The situation for hydrochloric acid (HCl) is similar. The major sources appear to be marine air (an uncontrollable source) and fossil fuel combustion (a source whose HCl emissions might be controlled to some degree, but are not controlled at present). No major long-term changes in atmospheric HCl levels seem likely to occur. In the case of the organic acids, source flux data is extremely scant. The sources are not well understood at all, but appear to include combustion of hydrocarbons, production by atmospheric hydrocarbon reactions, and natural emissions from vegetation. The atmospheric concentrations of the organic acids are probably relatively stable.

Susceptibility of Metals

Many common metals and alloys are degraded upon contact with a number of the species contained in precipitation and listed in Table 3. It is not appropriate here to discuss those interactions in detail, but it is useful to briefly summarize metallic susceptibilities. This is done in



FIG. 7—Boxplot comparison of trends in annual mean nitrogen dioxide concentrations at 177 U.S. sites, 1975 to 1983. Most of these sites are in urban areas. (Reproduced from Ref 10.)

Metal	H₂SO₄	HNO ₃	нсоон	HCI	NH ₃
Copper	x		x	x	x
Bronze	х		х	x	х
Brass	x		x	x	х
Silver	x	x	x	x	х
Iron	x		x	x	х
Lead	х		x	x	х
Tin	x			x	х
Zinc	х		x	x	х
Nickel		x	x	x	
Aluminum	х		x	х	х

 TABLE 4—The potential for degradation of metals by various atmospheric species in precipitation.^a

"Adapted from Ref 9. An x indicates that the metal suffers some degradation upon interaction with the atmospheric species.

Table 4, which is derived from a more detailed study described in [9]. With few exceptions, the materials are capable of degradation by sulfuric acid, formic acid, hydrochloric acid, and ammonia. Some are susceptible to nitric acid as well.

While the sensitivity of metals to specific corrodents may be a matter of record, the magnitude of that sensitivity generally is not. As a consequence, even if the exact nature of exposure to corrodents in precipitation is known, the kinetic data needed to make projections of the material's degradation is generally unavailable. One of the current challenges to corrosion scientists is to derive these damage functions for a variety of material-corrodent combinations.

Conclusions

Precipitation in its various forms contains a number of potentially corrosive constituents, and the occurrence and duration of precipitation and the concentrations of corrodents within it show wide ranges of variability. In addition to short-term trends and patterns, longer-term scenarios can be drawn for the atmospheric concentrations of some of the corrodents. Any study of the degradation of materials exposed to the atmosphere must therefore concern itself with the full spectrum of corrosive species, with their wide variabilities, and with the susceptibility of many metals to them.

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Test Methods

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A Study of the Effects of Dry and Wet Deposition on Galvanized Steel and Weathering Steel: A Three-year Field Exposure

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ABSTRACT: At an exposure site located at Research Triangle Park, NC an automatic covering device was installed to partition the effects of dry and wet deposition on the corrosion of galvanized steel and weathering steel samples. Mass loss was used as the measure of corrosion of both metals. Meteorological and air quality were recorded continuously during the 36-month exposure study and evaluated to eliminate errors and to estimate missing data. Models were derived to describe the corrosion of galvanized steel and weathering steel. Rainfall was found to be a significant factor for the corrosion of both metallic materials.

KEY WORDS: corrosion, galvanized steel, weathering steel, air pollution, acid rain, environmental effects

At a material exposure site located at the Research Triangle Park, NC in 1982, the Environmental Protection Agency (EPA) began a study on the effects of dry and wet deposition on panels of galvanized steel and Corten A weathering steel. An automatic covering device was used at the site to partition the effects of dry and wet deposition during exposure of these materials. This information is needed to determine the relative effects of gaseous and acid rain pollutants. Two sets of panels were prepared for each material. One set of panels was covered by the automatic device only during each rain event. The other set of panels was boldly exposed to both dry and wet deposition at the site. Corrosion of the metals was determined from mass loss and gain measurements. Air quality and meteorological parameters were continuously monitored and reported as hourly averages at the site. Collections of rain and particles are also analyzed and reported. Multiple regression techniques were used to determine the factors that were statistically significant. Models were developed to explain how dry and wet deposition factors affect the corrosion rates of galvanized and weathering steels.

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Experimental Procedure

Material Selection and Preparation

Both weathering steel and galvanized steel are used for exterior applications. Weathering steel was developed for use in unpainted architectural and structural designs. The weathering steel selected for exposure in this study was Corten A, a product of U.S. Steel Corporation. Commercial grade 20 gauge galvanized steel sheet with an approximately $25-\mu m$ zinc coating was selected for exposure.

For both metals, 10×15 cm panels were sheared from sheet stock. Panels of both metals were individually identified by a code stenciled lightly on the ground exposure side. Prior to field exposure, the galvanized steel panels were cleaned by immersion for approximately 2 min in 10% by weight ammonium chloride solution at a temperature of 60 to 80°C [1]. The weathering steel panels were immersed in Clark's solution until the scale was visually removed according to ASTM Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens G 1-81. Panels of both metals were rinsed first in deionized water and then in methanol to remove moisture. After drying, each panel was weighed to 0.1 mg.

Exposure Procedure

The weathering steel and galvanized steel panels were exposed at 30° to the horizon facing south according to ASTM Recommended Practice for conducting Atmospheric Corrosion Tests on Metals G 50-76. Triplicate samples were exposed for periods of 6, 12, 24, and 36 months. The weathering steel was also exposed for 18 and 30 months. The six-month panels were continually replaced with new panels to study the effects of dry and wet deposition during winter and summer months.

Two complete sets of the weathering steel and galvanized steel panels were exposed at the Research Triangle Park, NC site. An automatic device triggered by the rain sensor on a rain bucket collector was used to cover one set of panels only during each rain event. This set of panels was exposed primarily to dry deposition. The other set of panels was not covered during rain events and was exposed to both dry and wet deposition.

Panels were weighed before removing the corrosion products. They were then cleaned according to the procedures used before exposure. However, it was necessary to immerse and weigh each panel of both metals several times to ensure removal of the corrosion products. The weights were corrected for loss of base metal in accordance with ASTM Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens G 1-81. Each of the panels were weighed to 0.1 mg. The masses of both the total corrosion loss and corrosion product film were obtained.

Environmental Monitoring

The environmental parameters, specifically air quality, including particles, meteorology, and rain chemistry, that are being monitored at the Research Triangle Park, NC exposure site along with the reporting format are shown in Table 1.

Ambient concentrations of sulfur dioxide (SO_2) , ozone O_3 and oxides of nitrogen (NO_x) $(NO_2$ and NO) are continuously monitored at the site by instruments that approved by EPA as designated reference or equivalent methods. A technique for intermittent sampling of particles over a 7 to 10 day period using a dichotomous and high-volume sampling system was developed for characterizing particulate into coarse (2.5 to 10 μ m), fine (<2.5 μ m), and total mass size fractions. Sampling of particulate was initiated in early 1985 at the site. The meteorological parameters are continuously monitored by a Climatronics Weather Station. An Aerochem Metrics wet and dry precipitation collector is used to collect monthly rainfall for analysis.

Parameters	Reporting format
Air Quality	
continuous SO ₂ , NO, NO _x , NO ₂ , O ₃	hourly average
particulate chemistry: mass, size,	
composition	weekly analysis
Meteorology	-
weather: wind speed (WS) and wind	
direction (WD), temperature (T),	
relative humidity (RH),	
precipitation, solar radiation	hourly average
Rain chemistry	
pH	
cations	
anion	monthly analysis

TABLE 1—Environmental parameters measured at Research Triangle Park, NC exposure sites.

Through a contract with EPA, the Research Triangle Institute (RTI) operated the air quality, meteorology, and rain chemistry instrumentation and insured the quality of the environmental data. Northrop Services Inc. (NSI) operated the particle sampling device and provided the analysis. In addition to the routine calibration checks that RTI and NSI performed on the environmental systems at sites, an independent system and performance audit was conducted annually.

Analysis of Environmental Data

The environmental database contained errors and missing hourly averages of air quality and meteorological data that occurred when monitoring instrumentation was either not operational or in need of calibration. A methodology similar to that previously reported [1] was used to make corrections to the environmental database. Climatological data from the Raleigh-Durham (RDU) Airport (about 8 km from the site) was used in this analysis of the meteorological data.

Dew point, which is one of the most important environmental parameters, was measured with a lithium chloride sensor for which the manufacturer specified an accuracy of only $\pm 3^{\circ}$ C. Averages during exposure periods from these data were consistently lower than averages of dew points for the same periods at the Raleigh-Durham Airport. In contrast there was very little difference in comparable temperatures. Calculated relative humidities using the raw RTI data were often less than 85% during periods of rain. From such calculations, the fraction of time that 85% relative humidity was exceeded was much less than expected. Because of this systematic bias, all of the dew point data were adjusted by adding 1.1°C. This change approximately doubled the calculated times of wetness and eliminated rain-relative humidity inconsistencies. In the summer of 1985, a cooled mirror dew point sensor was added to the site.

Monthly total collections as well as hourly collections for each rain event were recorded at the site. Both sets of data were used in conjunction with the RDU Airport rainfall data to provide a corrected rainfall data base.

Pollutant Fluxes

The corrosion of galvanized and weathering steel is expected to be a function of the amounts of the pollutants reaching the metal surface and the moisture conditions of the surface. The amount of a pollutant deposited is the product of the ambient concentration and the deposition velocity. Deposition velocities were estimated from theory [2] and from wind speed data measured at the site. The following empirical relationship was developed from the more complex theoretical model:

$$u = 0.36 \ WS^{0.86} \tag{1}$$

where

u is deposition velocity in cm/sec, and WS is wind speed in m/sec.

Hourly deposition velocities, which were computed from Eq 1, were multiplied by hourly gaseous pollutant concentrations to obtain hourly fluxes. These values were summed over the exposure periods for different definitions of hours of wetness. (Relative humidities exceeded 80, 85, or 90% when the dew point was greater than 0° C and when it was raining. Relative humidities were below the stated values as applicable.) Hourly relative humidities were calculated from the temperature and dew point data.

Atmospheric particle concentrations were not measured at this site until 1985. In February, weekly samples were begun using a dichotomous sampler and a *Hi-vol*. The size fraction ranges were approximately 0 to 2.5 micrometers diameter, 2.5 to 10 μ m, and 0 to about 100 μ m. The overall annual average concentrations for the size ranges were <2.5 μ m: 16.9 μ g/m³, 2.5 to 10 μ m: 10.6 μ g/m³, and total suspended particulate matter (TSP): 37.5 μ g/m³. There is just as much material above 10 μ m in the coarse mode fraction as there is below 10 μ m, indicating that the mass median diameter for this mode is 10 μ m.

Some exposures were divided into winter and summer months. The average concentrations for the fine and coarse modes were for winter, $14.5 \ \mu g/m^3$ and $17.7 \ \mu g/m^3$, and for summer, $18.6 \ \mu g/m^3$ and $22.0 \ \mu g/m^3$, respectively. The average deposition velocity for the fine mode is expected to be < 0.02 cm/sec, while the deposition velocity of the coarse mode to a horizontal surface should be based on the terminal gravitational settling velocity. Assuming a mass median diameter of 10 μ m, a geometric standard deviation of 2, and a density of 2 g/cm³, an average deposition velocity of 1.66 cm/sec was calculated for the coarse mode. With these concentrations, deposition velocities, specimen angles, and exposure times, particle accumulations can be calculated. The coarse mode deposition is at least two orders of magnitude greater than the fine mode deposition.

Chemical analysis showed that nearly 20% of TSP is sulfate ions and 75% of that is fine. Only about 9% of the coarse is sulfate ions.

Theoretical Considerations

During atmospheric exposure, galvanized steel and weathering steel form surface films of corrosion products. These films tend to restrict the rate of corrosion by forming a protective surface layer. The rate of corrosion would then be diffusion-controlled and depend upon the thickness of the film. When the corrosion products of the film are insoluble and do not change during exposure, the corrosion-time function is expected to be parabolic ($C = \alpha \sqrt{t}$). However, many of the known corrosion products, particularly the carbonates, hydroxides, etc. within the film are soluble in acidic solutions. In environments where acidity such as acid rain, SO₂, etc. is present, dissolution of the protective surface film is a competing mechanism that accelerates the rate of corrosion. Under these exposure conditions, the corrosion-time relationship can be empirically expressed as [3]

C

$$=At^{n} \tag{2}$$

where

C is a measure of corrosion such as mass loss,

t is time, and

A and n are empirical coefficients. The n coefficient usually has a value between 0.5 and 1.0.

The mathematical solution to the differential equation describing the mechanism of competing formation and dissolution of the protective film is the transcendental function [2]

$$C = bt + a[1 - \exp(-bC/a)]/b$$
 (3)

which is equivalent to

$$C = bt + a/(dC/dt) \tag{4}$$

where

C and t are defined above,

dC/dt is the corrosion rate at time t,

b is the rate of dissolution of the protective film, which is a function of the rate of delivery of the reacting pollutants to the surface, and

a is a function of diffusivities through the film, which can also be affected by pollutants

The term, $a[1 - \exp(-bC/a)]/b$ represents the amount of metal in the corrosion product film. When bC/a is large, $\exp(-bC/a)$ approaches zero and Eq 2 becomes

$$C = bt + a/b \tag{5}$$

Equation 5 is linear with a/b being the intercept and b being the slope of the corrosion-time curve (corrosion rate).

Weathering Steel

Most of the corrosion products of weathering steel are retained in the film during the first few years of exposure. During the early corrosion stages of weathering steel, Eq 3 becomes:

$$C = bt + at/nC \tag{6}$$

where $dC/dt = nAt^{n-1} = nC/t$ (from the empirical relationship of Eq 2). If a/nC is greater than b, most of the corrosion products remain in the film and the corrosion-time function should be parabolic. Except when the protective film stays wet, the film becomes more protective with time. During extended periods of wetness, the corrosion resistance of weathering steel is not much better than carbon steels and is not recommended for use in humid environments.

Galvanized Steel

When exposed in a polluted environment, galvanized steel exhibits linear corrosion behavior. In nonpolluted environments, the corrosion-time curve may have some observable curvature during the first year of exposure. The linear corrosion behavior of galvanized steel indicates that the rate of formation of the protective film is equal to the rate of its dissolution. The complex basic zinc carbonate that forms in the protective film on galvanized steel can be dissolved during rain. The solubility of zinc carbonate is dependent on the concentration of CO_2 in the solutions

[4], which is dependent on the atmospheric concentration of CO_2 . As the temperature increases, the solubility of carbon dioxide (CO_2) in water decreases [5].

Following a textbook example for the thermodynamics of metal carbonates [6], it can be shown that the overall reaction simplifies to:

$$ZnCO_{3(c)} + H_2O_{(1)} + CO_{2(g)} = Zn^{2+} + 2HCO_3^{-}$$
(7)

The equilibrium equation assuming unit activity for both zinc carbonate and water and an ion balance is:

$$Zn^{2+} = (K[CO_{2(g)}]/4)^{1/3}$$
 (8)

where Zn^{2+} is gm moles/L and $[CO_{2(g)}]$ is atmospheres of CO₂ in air.

From thermodynamic considerations [6] and solubility data [4,5], the equilibrium constant K is related to temperature by the relationship calculated with thermodynamic data from Table 2 as follows:

$$K = \exp(-126.6 + 9583/T + 13.59 \ln T)$$
(9)

where T is the absolute temperature in degrees kelvin.

The corrosion of zinc in molecules is reported to be stoichiometrically equal to the amount of SO₂ in molecules deposited during periods of wetness (i.e., dew) [7,8]. Thus, 0.00143 μ m of zinc are expected to corrode for each μ g/cm² of SO₂ deposited.

Results

Environmental Data

The environmental data for the 36-month exposure period are given in Table 3. Similar averages were calculated for all exposure periods.

It should be noted that values for both SO_2 concentration and deposition velocity are significantly lower during periods of wetness than are the averages for total time of exposure. The deposition velocities and fluxes are the calculated turbulent movement toward the specimen

Compound	ΔH°	S°	Ср
ZnCO _{3(c)}	-194.2	19.7	19.14
H ₂ O ₍₁₎	-68.3174	16.716	17.973
$CO_{2(g)}$	-94.0518	51.061	8.87
$CO_{2(ac)}$	-98.90	28.08	18ª
H ₂ CO _{3(aq)}	-167.22	44.8	36.8
HCO ₃ -	-165.39	21.8	31ª
$CO_{3}=$	-161.84	-13.6	25.2ª
Zn ²⁺	-36.78	-26.8	11

 TABLE 2—Thermodynamic functions for zinc carbonate solubility.

NOTE: Related thermodynamic equations:

 $\ln(k) = -\Delta F_T / RT, \ \Delta F_T = \overline{\Delta} H_T - T\Delta S_T, \ \Delta H_T = I_H + \Delta C_P T, \\ \Delta S_T = I_S + \Delta C_P \ln T, \ \text{and} \ I_H = \Delta H_{298}^\circ - 298.2 \ \Delta C_P, \ I_S = \Delta S_{298}^\circ - 5.7 \ \Delta C_P.$

at 25°C from Weast, R. C. and Astle, M. J., CRC Handbook of Chemistry and Physics, 63rd Ed., CRC Press, Inc., Boca Raton, FL, 1982.

"Calculated from Kopp's Rule modified to be consistent with CO₂ solubility as a function of temperature. H = 5.8, O = 7.3, and C = 3.4.

			A	Averages fo	r		
				When	Wet ^a		
		RH >	80%	RH >	85 %	RH >	90%
Factor	Total Time	with rain	without rain	with rain	without rain	with rain	without rain
Temperature, °C	15.1	15.1	15.0	14.6	14.6	13.9	13.7
Dew point, °C	8.7	13.5	13.5	13.4	13.5	13.0	13.0
Relative humidity, %	69.1	90.5	90.8	92.4	93.1	94.3	95.6
Windspeed, m/s	1.59	1.17	1.15	1.17	1.14	1.19	1.12
Deposition velocity, cm/s	0.51	0.39	0.38	0.39	0.38	0.40	0.38
$SO_2, \mu g/m^3$	8.0	5.0	5.0	4.8	4.8	4.5	4.4
NO _x as NO ₂ $\mu g/m^3$	42.7	46.4	46.6	46.4	47.2	47.6	48.9
SO_2 flux, $\mu g/cm^2 y$	144	66	65.1	63.5	61.7	61.9	58.2
NO _x flux, $\mu g/cm^2 y$	434	370	367	371	366	380	374
Fraction when wet		0.347	0.340	0.277	0.266	0.200	0.184

TABLE 3—Average environmental conditions for a 36-month exposure period.

"Dew point is greater than 0°C.

surface and not net diffusion. When surfaces are dry, SO_2 will absorb until a monolayer is built up [8]. After that, the net flux will be zero (movement away equals movement toward). During wetness periods, SO_2 is either consumed to form a sulfate or catalyzed to nonvolatile sulfuric acid so that the net flux approaches the turbulent flux toward the surface. The drop in SO_2 concentration during periods of wetness is evidence that the rate of removal from the atmosphere is much faster than it is when dry. In contrast, NO_x concentrations do not change significantly because the net flux is extremely low, even during periods of wetness [9].

The average rain chemistry and loadings on specimens for the 36-month period are given in Table 4. Similar averages were calculated for all exposure periods. The range of concentrations varied by less than a factor of 2.5. The average pH ranged from 4.19 to 4.58.

Ion	Concentration $\mu \text{ mol/L}$	Specimen Loading ^a μ mol/cm ²
H+	38.20	5.38
Ca ²⁺	2.37	0.33
Mg ²⁺	1.39	0.20
K∓	0.77	0.11
Na ⁺	9.25	1.30
NH₄ ⁺	10.47	1.47
NO ¹ ₃	16.35	2.30
Cl-″	11.66	1.64
SO₄	18.55	2.61
PO ₄	0.10	0.01
pН	4.42	

TABLE 4—Average rain chemistry and loadings on weathering steel and galvanized steel corrosion specimens for a 36-month exposure.

"Rain is assumed to fall vertically on the skyward side of the specimens mounted at a 30° angle to the horizontal. Thus, the average loading for both sides is $0.5 \cos 30$ times the loading on a skyward horizontal surface.

Weathering Steel

The results for weathering steel are presented in Table 5. The samples started in the winter corroded more than those started in the summer. The covered samples corroded more than the uncovered samples exposed to rain. The ratio of weight of metal loss to weight of rust remaining on the samples increases with exposure time. This indicates that some of the rust is removed during exposure. Since the second term in Eq 3 represents the amount of metal in the rust film, a simple linear relationship for the above data exists:

$$C/t = b + kR/t \tag{10}$$

where

R is the weight of rust, and

k is the ratio of the metal in rust to the rust weight.

Simple linear regression results for the four different sets of data in Table 5 are presented in Table 6. An analysis of variance indicates that the values for k have a relatively low probability of being statistically different from each other. The differences, however, are consistent with expected differences in levels of hydration. Assuming the oxide is ferrous oxide (Fe₂O₃), the k values are equivalent to respective levels of hydration for covered specimens of 96.7% for uncovered winter specimens of 90.6%, and for uncovered summer specimens of 76.5%. Covered same

Starting Season		Exposure years	Covered			Uncovered			
	Starting Date		Metal Loss	Rust Remaining mg/cm ²	Ratio	Metal Loss	Rust Remaining mg/cm ²	Ratio	
Winter	10/19/82	0.543	10.579	16.605	0.637	9.081	14.811	0.613	
		1.044	16.450	24.752	0.665	15.447	23.482	0.657	
		2.052	23.293	31.506	0.739	19.339	27.258	0.709	
		3.038	27.357	34.854	0.785	22.245	29.529	0.753	
	11/04/83	0.493	9.734	16.031	0.607	8.512	14.013	0.607	
	11/06/84	0.986	17.138	24.491	0.700	14.066	21.277	0.661	
Summer	5/05/83	0.501	9.428	15.538	0.607	9.060	15.052	0.602	
		1,510	16,297	24.227	0.672	13.614	20.620	0.660	
		2,494	22.955	30.714	0.747	17.577	24.486	0.715	
	5/02/84	0.515	9.903	16.195	0.612	9.182	14.995	0.612	

TABLE 5—Weathering steel	corrosion	results
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TABLE 6—Corrosion-rust regression results.

Exposure							
			b		k		
	Starting Season	Value	Standard Error	Value	Standard Error	Variation Explained (fraction)	
Covered	Winter Summer	3.292 2,546	0.825 0.297	0.5270 0.5270	0.0340 0.0122	0.9837 0.9989	
Uncovered	Winter Summer	2.343 1.512	0.450 0.187	0.5354 0.5556	0.0209 0.0083	0.9940 0.9996	

ples can accumulate hydroscopic pollutants, which can keep them wet more often and increase the chances for hydration. Summer temperatures should dehydrate the uncovered samples that have been washed by rain. The k values in Table 6 were used to calculate the amount of iron remaining in the film.

The film dissolution rate b for any one set of environmental conditions is:

$$b = (C - kR)/t \tag{11}$$

The diffusivity through the film (a) for a set of conditions is:

$$a = bkR/(1 - \exp(-bC/a))$$
(12)

Thus, with C, k, and R known, the potentially environmentally sensitive coefficients a and b can be calculated for each exposure. The results are given in Table 7.

Although both b and a vary considerably, a/b, which represents the equivalent amount of iron in the film when a constant corrosion rate is reached, is fairly constant. This may indicate that the rate of dissolution is controlled by the rate of diffusion of a soluble ion through the film. With iron in the film and total metal loss expressed as micrometers, a best fit between the two yields a constant k of 0.5318 and an a/b of 41.49 with 0.997 of the variance explained. The value for k is equivalent to that of 93.2% hydrated Fe₂O₃ and the value for a/b is equivalent to film weight when a constant corrosion rate of 60.07 mg/cm² is reached.

Individual values for a and b were recalculated using a k of 0.532 for all conditions. As expected, the resulting ratios of a/b were much closer to being constant than in Table 7. To conform to the best fit relationship, both values were adjusted by a factor $(a/b/41.49)^{0.5}$. The value for a was divided by the factor and the value for b was multiplied by the factor. The results are given in Table 8.

Galvanized Steel

The results of the galvanized steel corrosion measurements are given in Table 9. The uncovered samples corroded more than the covered samples, but the corrosion product film remaining on the samples is about the same for both conditions. There is no apparent difference between samples started in winter and in summer.

The covered and uncovered data in Table 9 were regressed on Eq. 10, resulting in b coeffi-

Starting Season		Exposure, Years	Covered			Uncovered		
	Starting Date		b µm∕year	a μm²/year	a/b	b µm∕year	a μm²/year	a/b
Winter	10/19/82	0.543	4.191	154.2	36.79	2.887	116.6	40.39
		1.044	4.094	188.4	46.02	3.682	167.3	45.44
		2,052	4,140	175,3	42.34	3,067	126.8	41.34
		3.038	3.772	160.1	42.44	2, 98	108.8	38.88
	11/04/83	0.493	3.188	148.3	46.52	2.795	113.4	40.57
	11/06/84	0.986	5.421	209.1	38.57	3,625	146.3	40.36
Summer	5/05/83	0.501	3.022	136.9	45.30	2.738	177.1	46.42
		1.510	2.939	126.8	43.14	2,281	.9.6	39.28
		2.494	3.450	141.9	41.13	2.346	85.7	36.53
	5/02/84	0.515	3.259	146.3	44.89	3.050	125.6	41.18

TABLE 7-Calculated dissolution rates and diffusivities."

"Steel density (7.7 g/cm³) used to convert to equivalent thickness loss.

			Cov	vered	Uncovered	
Starting Season	Starting Date	Starting Exposure, Date Years		a_1 μ m ² /year	b ₁ μm/year	a_1 μ m ² /year
Winter	10/19/82	0.543	3.947	163.7	2.848	118.2
		1.044	4.311	178.9	3.853	159.9
		2.052	4.225	175.3	3.061	127.0
		3.038	3.815	158.3	2.709	112.4
	11/04/83	0.493	3.376	140.1	2.763	114.6
	11/06/84	0.986	5.226	216.8	3.575	148.3
Summer	5/05/83	0.501	3.158	131.0	2.896	120.1
		1.510	2.997	124.3	2.220	92.1
		2.494	3.435	142.5	2.202	91.4
	5/02/84	0.515	3.390	140.6	3.039	126.1

TABLE 8-Best fit film dissolution rates and diffusivities."

"k equals 0.5318 and a_1/b_1 equals 41.49.

TABLE 9-Galvanized steel corrosion results.

Starting Season			Covered			Uncovered			
	Starting Date	- Exposure, Years	Metal Loss	Rust Remaining mg/cm ²	Ratio	Metal Loss	Rust Remaining mg/cm ²	Ratio	
Winter	10/19/82	0.543	0.143	0.181	0.793	0.238	0.181	1.315	
		2.052	0.432	0.392	1.101	0.885	0.406	2.177	
	11/04/83	0.493	0.241	0.291	0.826	0.342	0.225	1.516	
Summer	5/05/83 5/02/84	0.501 0.515	0.200 0.158	0.342 0.156 0.226	1.280 0.700	0.216 0.308	0.131 0.293	1.645 1.051	

cients that were significantly different but values for k that were not. A dummy variable for the covered/uncovered condition was added to the equation, and multiple linear regression was applied to the combined data to yield a single value for k of 0.6191 with a standard error of 0.1074. A basic zinc carbonate film with a composition of $2\text{ZnCO}_3 \cdot 3\text{Zn}(\text{OH})_2$ has a zinc-to-film weight ratio of 0.5955.

This value and the data in Table 9 were used to calculate the individual values for dissolution rates (b) and diffusivities (a) in the same manner as was done for the weathering steel. The results are in Table 10.

Unlike weathering steel, the ratio a/b for galvanized steel is not constant. The ratios are less for the uncovered samples than for the covered samples. The solubility rates (b) and the diffusivities (a) are greater for the uncovered samples than they are for the covered samples. There appear to be no differences associated with starting season. This could be the result of the effects of individual sets of conditions, experimental error, or a missing season effect.

Starting Season	Starting Date	Exposure, Years	Covered			Uncovered		
			b μm/year	a µm²/year	a/b	b µm∕year	a µm²/year	a/b
Winter	10/19/82	0.543	0.092	0.0308	0.334	0.336	0.0601	0.179
		1.044	0.159	0.0624	0.392	0.430	0.0889	0.207
		2.052	0.135	0.0590	0.436	0.439	0.1531	0.349
		2.979	0.138	0.0681	0.494	0.400	0.1638	0.410
	11/04/83	0.493	0.191	0.0927	0.487	0.589	0.1233	0.209
	11/06/84	0.926	0.116	0.0675	0.579	0.377	0.1255	0.333
Summer	5/05/83	0.501	0.299	0.0467	0.156	0.385	0.0457	0.119
	5/02/84	0.515	0.064	0.0429	0.667	0.363	0.1236	0.340

TABLE 10-Calculated dissolution rates and diffusivities for galvanized steel.^a

"Zinc density (7.14 g/cm³) used to convert to equivalent thickness loss.

Discussion

Weathering Steel

In Table 8, dissolution rates (b_1) and diffusivities (a_1) are related by a constant (a_1/b_1) equal to 41.49 micrometers. Thus, environmental factors that affect one coefficient will affect the other proportionately.

Multiple linear and nonlinear regression techniques were used to determine which environmental parameters can be statistically related to the calculated diffusivities through the corrosion film. Variables considered in both stepwise and selected combinations were pollutant fluxes, total exposure time, fraction of time when wet, rain and rain constituent fluxes, a temperature factor (1/(273.16 + dew point)), and two dummy variables representing exposure condition and starting season. A one was used for covered samples and a zero for the uncovered. Similarly, a one was used for winter samples and zero for the summer samples. The best fit of the data in Table 8 has the form:

$$\ln(a_1) = k_0 + k_1 Sn - k_2 Rn - k_3 t^2 - k_4 / T_{dp}$$
⁽¹³⁾

where

Sn = the starting season dummy variable,

 $Rn = rain flux cm/cm^2/year$ (the average of the upper and lower surfaces),

t = exposure time in years,

 T_{dp} = average dew point in °K, and

 k_i = regression coefficients.

The regression results are given in Table 11. Because of strong covariances between these and other environmental factors, excluding one or more of the above in a stepwise regression makes other factors statistically significant. For example, particulate matter flux was strongly covariant with dew point average and rain sulfate flux was strongly covariant with rain flux. When rain and dew point were excluded from the regression, these two factors became statistically significant. The variability explaining fraction, however, was not as good. Fluxes of pollutant gases and fraction of time when wet were not statistically significant in any combination of regressions, possibly because of low variability between exposure periods or the magnitude of the experimental measurement error.

350 DEGRADATION OF METALS IN THE ATMOSPHERE

If the assumption of a constant a/b is valid, then regressions of $\ln(b)$ and $\ln(a)$ from data in Table 7 versus environmental factors should produce results similar to Table 11. These regressions revealed that the same variables were statistically significant, and the values of their coefficients were not significantly different. As expected, the k_0 value for the $\ln(b)$ regression was different from the k_0 values for the $\ln(a)$ and $\ln(a_1)$ regressions. The degree of fit was not as good for the $\ln(b)$ and $\ln(a)$ regressions as it was for the $\ln(a_1)$ regression.

These statistical relationships can be explained in terms of possible physical effects on the diffusivity through the oxide film. Both the sign and magnitude of the temperature effect is consistent with expectations. The value is comparable to an activation energy for diffusion of 6458 cal/gm mole/°K. Rain can wash away soluble constituents that could otherwise become part of the rust film. These constituents could increase diffusivity. The structure of the oxide film is expected to change to a more stable form with time. This change should be accompanied by a decrease in diffusivity. The winter/summer initial exposure effect could be related to this process. Higher summer temperatures may favor the formation of a more stable oxide with a lower diffusivity than a winter formed oxide.

The values in Table 11 can be used to calculate the coefficients for dissolution rate and diffusivity. These in turn can be used to calculate the amount of metal in the film and the total metal loss for each exposure period.

Galvanized Steel

The anodic reaction of the zinc corrosion process occurs at the metal/corrosion product film interface. The cathodic reaction most likely occurs at the outer surface of the film where oxygen and water are readily available. The rate controlling factor is the diffusion of ions through the film. Not only diffusivity but also film thickness control this process. The thinning of the corrosion product film by dissolution, therefore, increases the corrosion rate of zinc.

A constant corrosion rate is reached when the rate of formation of the film is equal to the rate of dissolution of the film. After three years of exposure in this relatively clean environment, the covered samples had developed a film thickness that was about 80% of the calculated steady state thickness, while the uncovered samples had reached nearly 98% of their calculated steady state value. In highly polluted environments, the steady state film thicknesses will be very small and the corrosion time curves will become linear in a relatively short time.

Sulfur dioxide gas can deposit on the dry surface during the day until the surface is saturated and then react at night when the surface is wet with dew. The rate of deposition is assumed to be a monolayer per day on all of the surface area including the accumulated additional surface area associated with deposited particulate matter. Since rain washes off course mode particles, only the covered samples have accumulated additional surface area upon which SO_2 can deposit during dry periods.

When the surface is wet, sulfur dioxide flux is controlled by the concentration and the calculated deposition velocity of the gas phase.

Coefficient	Value	Standard Error	t Statistic	Probability
k ₀	16.2002			
k,	0.3894	0.0579	6.725	< 0.0001
k ,	-0.005167	0.000817	-6.324	< 0.0001
k ₃	-0.0190	0.0069	-2.775	0.0142
k 4	-3249.14	901.71	-3.603	0.0026

TABLE 11—Regression results of $\ln(a_i)$ versus environmental factors (Eq 13).

Sulfates can be delivered to the surface in particulate matter and in rain. Both can be assumed to fall vertically on the upper surface of the 30° angle specimens.

Assuming stoichiometric reactions with the film, zinc dissolution rates for each of the four delivery mechanisms can be calculated. Assuming 0.0003 atmospheres of CO_2 in the air, the solubility of zinc carbonate can also be calculated. This was done and the theoretical dissolution rates for each exposure period and condition are compared with the observed values in Table 12.

The regression techniques used to analyze the weathering steel data were also applied to the galvanized steel data. Because there was not a definite relationship between solubility rates and diffusivities in galvanized steel as there was for weathering steel, the two coefficients were analyzed separately.

The best fit of the solubility rate data was obtained with a simple linear regression on the rain solubility rate based on the calculated solubility of zinc carbonate. The independent variable was calculated using Eq 8 and 9 assuming 0.0003 atm CO_2 in the air and that rain falls vertically on the upper side of 30° angle specimens. Average dew point temperature in degrees Kelvin was used to calculate the equilibrium constant in Eq 9. Measured rainfall was multiplied by 0.5 cos 30 and divided by the exposure time to get specimen surface rain flux. The fraction of the *b* variability explained by this single calculated factor (based on the measured variables of dew point, rainfall, and exposure time) is 0.851. The resulting coefficients for the equation:

$$b = b_0 + b_1 Sr \tag{14}$$

where

b and Sr = the total and rain solubility rates respectively, both expressed in micrometers of zinc per year, and

 $b_0 = b_1$ are the regression coefficients

are: b_0 equals 0.153, with a standard error of 0.021, and b_1 equals 0.304, with a standard error of 0.034. Factors that are highly covariant with this variable (such as the flux of the constituents

Starting Date	- ·	S	O_2	Sul	fate	CO ₂		Observed
	Exposure in years	Dry	Wet	TSP	Rain	Rain	Total	
Covered								
10/19/82	0.543	0.051	0.014	0.034			0.099	0.092
	1.044	0.059	0.010	0.039			0.118	0.159
	2.052	0.073	0.009	0.039			0.121	0.135
	2.979	0.085	0.008	0.039			0.132	0.138
11/04/83	0.493	0.050	0.011	0.034			0.095	0.191
11/06/84	0.926	0.057	0.005	0.039			0.101	0.116
5/05/83	0.501	0.052	0.005	0.043			0.100	0.299
5/02/84	0.515	0.052	0.011	0.043			0.106	0.064
Uncovered								
10/19/82	0.543	0.047	0.016	0.034	0.070	0.989	1.156	0.336
	1.044	0.047	0.011	0.039	0.088	0.813	0.998	0.430
	2.052	0.047	0.011	0.039	0.086	0.890	1.073	0.439
	2,979	0.047	0.010	0.039	0.080	0.814	0.990	0.400
11/04/83	0.493	0.047	0.013	0.034	0.084	1.374	1.552	0.589
11/06/84	0.926	0.047	0.006	0.039	0.068	0.648	0.844	0.377
5/05/83	0.501	0.047	0.005	0.043	0.107	0.628	0.830	0.385
5/02/84	0.515	0.047	0.013	0.043	0.083	0.663	0.849	0.363

TABLE 12—Theoretical contributions to dissolution rates (b), $\mu m/year$.

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in rain) were individually significant when this variable was excluded in a stepwise procedure. In each case, however, the degree of fit was not as good as it was using rain solubility as the independent variable.

The regression coefficient for the clean rain solubility is less than one, indicating that the residence time of the rain on the specimens is not sufficient for the reaction to reach equilibrium. This coefficient should also be applicable to the possible effects of sulfate in rain on film solubility.

None of the other calculated effects in Table 12 were statistically significant, probably because their theoretical contributions are relatively low and, with the exception of sulfate in rain, vary little from one exposure to another. The average total of all of the other theoretical effects, including 0.304 times the rain sulfate effects, is only 0.115. The standard deviation on these totals is only 0.012. There is a high probability that this average theoretical effect is the same as the regression intercept of 0.153 μ m per year. Under these circumstances, small but real differences can easily be masked by experimental error and not be statistically significant in regression analysis. These results provide credance to the calculated relative contributions of the various pollutant delivery mechanisms.

Although the diffusivities (a) are different for the covered and uncovered samples, based on regression analysis, the within-sample differences cannot be statistically associated with rain rates or pollution fluxes. The average diffusivity for the covered samples is $0.059 \ \mu m^2$ per year, with a standard error of 0.007. For the uncovered samples the average is $0.111 \ \mu m^2$ per year, with a standard error of 0.015. The presence of rain almost doubles the diffusivity through the corrosion product film.

Other environmental pollutants that were not measured in this study could also affect either or both the dissolution rate (b) and the diffusivity (a). Nitric acid and formaldehyde could contribute to the corrosion of zinc [9].

Conclusions

Mass gain and loss corrosion data for both weathering steel and galvanized steel are consistent with a theoretical model for corrosion based on competing mechanisms of film formation and dissolution.

For weathering steel, the dissolution rate is proportional to the diffusivity through the oxide film. Diffusivity is the corrosion rate controlling factor. Exposure to rain reduces the corrosion rate, possibly by washing away constituents that may increase diffusivity through the oxide. A statistically significant effect of temperature on corrosion rate is consistent with a diffusion controlled process.

The rate of corrosion of galvanized steel was increased by exposure to rain. The effect is proportional to the theoretically calculated solubility of zinc carbonate in water with carbon dioxide in equilibrium with atmospheric concentrations.

Possibly because the expected range of pollutant effects was within the range of experimental error, no statistically significant effects of pollution were determined for either weathering steel or galvanized steel. Exposures under more and larger ranges of pollutant fluxes are needed to show statistical significance.

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DISCUSSION

J. Friel¹—(discussion question)—Since $Zn_5(CO_3)2(OH)_6$ is the predominant solid corrosion product on the surface of galvanized steel after atmospheric corrosion, do you plan to investigate reactions that would lead to its formation?

J. Spence—(author's closure)—No plans have been made to specifically study the structure of the film. Mass loss/mass gain ratios, however, are consistent with the above composition.

V. Agarwala²—(discussion)—In your analytical description of the mechanism of corrosion of galvanized steel, you used a solubilization factor of ZnCO₃, H⁺, which did not add up to compare with numbers for corrosion protective behavior. Probably the lack of compliance is due to a lack of additional factors such as hydrolysis products of Ca_6^{2+} , Mg^{2+} and NH^{4+} , which you suggested do deposit in sufficient quantities. These pollutants will also produce acid (H⁺) and cause additional dissolution of ZnCO₃.

J. W. Spence—(author's closure)—It should be noted also that the solubility of $ZnCO_3$ only serves as a proxy for the solubility of a more complex basic $ZnCO_3$. The residence time for rain on the surface is probably not long enough for solubility to reach equilibrium.

Corrosion Monitoring of Shipboard Environments

REFERENCE: Agarwala, V. S., "Corrosion Monitoring of Shipboard Environments," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 354-365.

ABSTRACT: A corrosion monitoring system is developed to determine the corrosivity of naval environments. It consists of a sensor (dissimilar bimetallic couples) and a galvanic current recording system (zero resistance ammeter). The data recording equipment is designed to monitor shipboard environments continuously on a long-term basis. Initially, a database was created from these sensors using accelerated laboratory environmental chambers. Corrosion monitor data, recorded on naval ships and aircraft carriers during their deployment at sea, are analyzed and assessed with respect to the laboratory database. The results show a direct relationship between the sensor output and the corrosivity of the constituents present in the environment.

KEY WORDS: corrosivity monitoring, marine atmosphere, naval environment, shipboard testing, galvanic sensors, aircraft carrier, accelerated laboratory testing, current transients

The corrosion problems of naval systems are very severe and varied. In particular, shipboard (aircraft carrier) environments are extremely damaging; sulfur from the carrier stack gases combined with sea spray provides a uniquely hostile environment. It has been characterized as the most severe of all atmospheric environments, marine and industrial included [1,2]. The Navy, ASTM and Aluminum Association interlaboratory testing program concluded that the aircraft carrier environment was twice as aggressive as the seacoast environment at Point Judith, RI [2]. These observations were based on the comparison of industrial and marine atmospheres with that of the shipboard environment (cruising) in the Mediterranean. However, fleet messages report that the Mediterranean environment (climate) is a lot less severe than that of the Indian Ocean, particularly in the monsoon season.

The theater of operation and the climate play a unique role in the corrosivity of the environment aboard a naval carrier. The environments of the Persian Gulf, Mediterranean Sea, and Indian, Atlantic and Pacific Oceans are quite different from each other and most certainly more severe than the coastal environments of the American continent. In particular, the climate during the monsoon periods, from May to September, in the Indian Ocean has been reported as extremely severe. The changing weather patterns from day to night create a continuous salt/ sand mist in the air and rise up to few kilometers above sea level. Temperatures up to 32° C, relative humidity >95%, and pollutants and soluble and particulate matter are the major constituents of these environments. Winds, rain, and ocean waves play a significant role also, and could accelerate or reduce the corrosivity of the environment. The situation is further aggrevated by the stack and aircraft exhaust gases produced from burning high-sulfur fuel aboard the carrier.

Currently the assessment of environmental corrosivity is made on the basis of data accumulated from outdoor, long-term exposure testing of metal panels. Laboratory tests such as salt

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fog or total or alternate immersion were primarily designed from projected figures obtained from these data to produce an accelerated laboratory test environment. Although these test methods have been quite successful in evaluating various materials, too often they have been used indiscriminately. In situations where rapid changes in the weather and/or activity of the equipment (aircraft start-ups, etc.) aboard the ship control the aggressive nature of the environment or the locations are inaccessible for panel testing, a correct evaluation of the corrosivity of the environment is not possible. The results obtained from any extrapolation of accelerated laboratory tests may be inaccurate at best, and deceptive at worst.

An assessment of the carrier stack gas dispersion was made on the flight deck of the USS John F. Kennedy, and the contours of concentration were plotted as shown in Fig. 1. The level of sulfur dioxide measured near the bridge at zero cross wind was recorded at as high as 300 ppm which decreased to approximately 60 ppm near the edge of the flight deck. The least concentration of sulfur dioxide measured at any time was 12 ppm about 30 m from the bridge. A typical stack soot analysis of various conventional fuel carriers yielded pH in the range of 2.4 to 3.0, and the sulfate ion concentration varied significantly, i.e., from 11 to 33% of the soot weight. Generally, the size and weight (including the aircraft aboard) of the vessel contributed to these differences.

Experimental Procedure

The approach to characterizing the shipboard environment was based on: (1) the use of a monitoring sensor to quantify the corrosion severity, and (2) the exposure of test panels (coupons) for a qualitative assessment of corrosivity in both the shipboard and simulated laboratory environments. The shipboard environment is usually that of the aircraft carrier during a mis-



DOWNWIND DISTANCE - FEET

FIG. 1—A contour map of sulfur dioxide dispersion from stack on a typical aircraft carrier.

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sion in the waters of the world and in almost all seasons. The accelerated laboratory test environments were primarily salt fog chambers containing the following: (1) 5% sodium chloride (NaCl) spray, (2) 5% NaCl spray + sulfur dioxide (SO₂), and (3) synthetic seawater spray + SO₂. Both the metal test panels and the corrosion monitoring sensor were exposed to these environments and data collected over time.

Sensor Design and Instrumentation

The sensor was developed using well known principles of galvanic corrosion [3]. The design of the sensor has been evolving almost every year. The two latest designs developed by the author are shown in Fig. 2. The sensor in Figure 2A is an omnidirectional cylindrical probe made in a conventional way reported elsewhere [4]. The second sensor (Fig. 2B) is made from thermoplastically set sandwitches of steel/PTFE/copper/PTFE/steel/. . . . sheets, $1.0 \times 10 \times 25$ cm in size. The PTFE sheets used were coated with thermoplastic resin (an epoxy system) and could be easily compiled into a deck of 7 or 8 plates each of copper and steel and hot-squeezed under a hydraulic press. When this was set and cured, it was cut into 2-cm width sensors to provide an exposed (edge) surface area of approximately 20 cm². A hole was drilled at either end of this sensor to run a bus wire for connecting similar metal plates. Note the array of copper and steel plates was arranged during the sandwitch operation so that only similar metal plates (copper) were extending on one end and slightly recessed at the other; whereas the other metal plates (steel) were slightly recessed at this end but extended on the other end. The bus wires from the ends of the sensor provided the leads for a zero-resistance ammeter. With this method a number of sensors were fabricated in one attempt, easily and economically. The whole assembly was then potted to environmentally seal the leads and the top and bottom plates in an epoxy resin.

The galvanic cell current output from the sensor was recorded on a continuous basis using the data logging device shown in Fig. 3. The device consists of a zero resistance ammeter (ZRA), an analog to digital (A-D) converter, and a data logger. The ZRA was put together by using a potentiostat in which the voltage between the working (W) and reference (R) terminals was set to zero, and a known standard resistor was connected between the reference (R) and counter (C) terminals to measure the galvanic current as an IR (potential) drop for amplification and subsequent recording. The data logger used was programmable to record sensor output every 60 min for up to six months during exposure. The choice between the R and C resistors was such that it



FIG. 2—Corrosivity monitoring sensors: (a) omnidirectional, (b) thermoplastically set flat.



FIG. 3—A schematic and a photograph of a data logging device for monitoring sensor output.

could give a current range of 1 μ A to 1 mA in naval environments. A photograph of such a generic monitoring system is shown in Fig. 3.

Theoretical considerations of galvanic corrosion current measurements have been described elsewhere [4, 5, 6] and probably the best explanation of how a galvanic couple behaves in a corroding system is offered by the mixed potential theory [7]. For the present, it has been assumed that the cathodic metal (copper) behaves more like an oxygen depolarizer and undergoes the least corrosion. The extent to which steel polarizes is primarily dependent upon the following important environmental factors: temperature, relative humidity, oxygen concentration, and the ionic and particulate (i.e., salts, acids, gaseous, and carbonaceous matter) content of the atmosphere. In other words, the output of this sensor (galvanic couple) will be dependent upon these environmental parameters. Experimentally, the observed galvanic current values will be directly related to the corrosive nature of the environment.

In an earlier experimental program [4], the applicability of the corrosion monitoring sensor was pursued analytically under three different exposure conditions: (1) the continuous highhumidity (near 100% relative humidity) environment, (2) the accelerated laboratory corrosion test environment, and (3) to some extent in the naval aircraft environment. A number of galvanic couples were used. Copper/steel sensors provided the most reproducible results without much loss of the anodic metal. Figure 4 shows the sensor output (current) transients for this couple in various simulated laboratory environments. The effects of environmental variables on the output of various sensors at steady-state have been summarized in Table 1.



FIG. 4—Current (output) transients of a copper/steel sensor exposed to various laboratory simulated environments.

TABLE I-The effects of environmental variables on output of various sensors (garvanic couples) as	TABLE	E 1 - Th	e effects oj	^f environmental	variables on	output of	various sensors	(galvanic	couples)	use
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	Sensor Output, μA^a								
Environment	Copper/Steel	Copper/Aluminum	Steel/Aluminum						
Moisture (100% RH)	0.01	0.01	< 0.01						
Moisture + chloride ^{b}	0.1	0.5	0.01						
Moisture $+$ SO ₂	1.5	3	0.5						
5% NaCl spray	7.5	8	1.5						
Moisture + HCl ^c	28	260	220						
5% NaCl spray $+$ SO ₂	140	80	7						
Syn. seawater $+$ SO ₂ $+$ soak cycle	120 to 300	80 to 200	15 to 30						

"Steady state values after 20 h of exposure.

^hChloride ions as carried by the air when purged through a 1% NaCl solution.

"HCl as carried by the air when purged through a 6M HCl solution.

Laboratory Environment

A test chamber of 100% relative humidity was created for the calibration of the corrosion monitoring sensor by passing compressed air through vessels containing deionized water. The humidity and temperature of the chamber were monitored continuously by a system manufactured by Thunder Scientific Corporation (Model HS-1CHDT-2R). In experiments in which chloride and acid were required in the chamber, the air bubbling vessels contained 1% sodium chloride (NaCl) and 6*M* hydrochloric acid (HCl) solutions respectively, instead of deionized water. With this procedure approximately 0.2 mg/L of NaCl and 4 mg/L of HCl could be present at any time in the chamber. The galvanic corrosion current-transients (dotted curves) shown in Fig. 4 represent the results of these test.

The accelerated laboratory corrosion testing of both the test panels and the corrosion sensors was carried out in a salt fog cabinet as shown in Fig. 5. The design of the cabinet interior was according to the requirements of ASTM Standard Method of Salt Spray (Fog) Testing. B 117-73, Appendix A1. A 5% NaCl solution was sprayed into the chamber as a continuous mist to simulate the ocean environment. To represent the naval ship or carrier environment, SO₂-laden salt fog was required in the test chamber. The sulfur dioxide gas was introduced in the cabinet for one h, four times a day, at a flow rate of 35 mL/min/m³ while salt fog was continuously sprayed. The rationale for these specifications has been reported earlier by Ketcham and Jankowsky [2]. The use of 5% synthetic sea salt in place of 5% NaCl was also studied and compared. It was determined that for steel (copper/steel sensor), both the environments were almost equally corrosive, but for the aluminum (copper/aluminum sensors), the sea salt environment was less severe.



FIG. 5—Photograph of a salt fog cabinet with provisions for metering sulfur dioxide periodically.

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Ship Environment

The selection of the ship environment was basically dictated by the availability of the vessel because of restrictions associated with military operations. However, efforts were made to select at least two types of carriers, conventional (oil fueled) and nuclear-powered, cruising on opposite sides of the globe (Pacific and Atlantic Oceans). A naval research ship, USNS Vanguard, was also used for the study because it was readily available and monitored.

For shipboard testing, the sensor was installed on either a radar tower about 6 m above the flight deck of the aircraft carrier or near the stack in the aft on the research ship (Fig. 6). The



FIG. 6—Photograph of the research ship USNS Vanguard showing the installation of a test rack and a sensor near the stack.

current measuring instruments were located in the radar room to isolate them from the flight deck. The sensitivity of the recording system was set low so that at high relative humidities (>85%), the output of the sensor was low $(1 \text{ to } 2 \mu \text{A})$. This way, the full-scale range setting on the recording system could measure up to $500 \mu \text{A}$. The sensor output is recorded for a period of six to eight months on the ships. Among the test panels used for the shipboard and laboratory testing, 7075-T6 aluminum alloy was the primary choice. This alloy has been a major structural material for aircraft because of its high strength, but has been known to corrode severely in naval environments. It suffers severe exfoliation corrosion and stress corrosion cracking in SO₂-containing salt fog environments. Thus, Al 7075-T6 alloy could serve as the best candidate material for evaluating environmental corrosivity in the naval systems.

Results and Discussion

Laboratory Study

The results, obtained from the simulated laboratory tests, have shown (Fig. 4) that after an initial surface conditioning of the sensor surface which could sometimes take 5 to 10 h, the output tends to become steady, and depending upon the environment present in the chamber, it takes an orderly relative position on the scale of corrosivity. Generally, it was found that as the corrosivity of the environment increased, the current measured by the sensor also increased. Corrosivity was independent of the sensor used as shown in Table 1, but differed in magnitude depending on corrosivity. The aluminum sensors showed an exception to this behavior in the environment containing HCI. The current output was greatest for the SO₂-containing environment. The copper/steel sensor was most responsive in sensitivity and reproducibility.

Based on the results obtained by the corrosivity monitoring sensor as summarized in Table 1 (Fig. 4), the environments could be arranged in the following order of increasing corrosivity:

moisture < (moisture + chloride) < (moisture + SO₂) < (5% NaCl spray)

$$< (5\% \text{ NaCl spray} + SO_2) < (synthetic seawater spray + SO_2 + soak cycle)$$

The increase in corrosivity from one environment to the next was almost an order of magnitude with the exception of one which contained HCl. The parallel tests on panels of AISI 1020 steel and 7075-T6 Al alloy exposed to these environments also exhibited similar order-of-corrosion behavior. In an earlier study by the author, the aluminum alloy test-panels exposed to these laboratory environments corroborated this order of corrosivity [8].

Shipboard Study

The current transient data of the aircraft carrier exposure test, from June to March 1978, during which the USS John F. Kennedy (carrier) was deployed to the Mediterranean, were recorded, condensed, and analyzed as shown in Fig. 7. The sensor used in this study was a flat copper/steel galvanic couple. As shown in Fig. 7, the sensor exhibited several periods of high corrosion activity (currents). In the first 40 days, it showed very little corrosion activity (less than $5 \mu A$), indicative of an average marine atmosphere similar to those obtained in 5% salt spray environment as shown in Table 1. Between 40 to 160 days, there appeared to be periods of wetness resembling the data obtained in salt spray and SO₂ test environment. However, in the last 100 days of deployment, a considerably high corrosion activity was recorded with sensor currents as high as 500 μA at some instants. These results correlated well with reports received from carrier personnel that the weather in the first four months of deployment was generally fair, whereas that of the last four months was characterized by storms and high seas.

Test specimens of the aluminum alloy exposed on the carrier also corresponded with the cor-

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FIG. 7—Current transients of a steel/aluminum sensor exposed to a conventional carrier environment (USS John F. Kennedy).

rosion monitor (sensor) data when inspected at intervals of four and eight months. The exfoliation or intergranular attack was slight at four months and severe after eight months' exposure (Fig. 8). Figure 8 also illustrates the behavior of 7075-T6 aluminum alloy on a nuclear powered carrier, the USS Nimitz. The differences between the two types of carriers were not significant in these tests because the USS Nimitz was stationed in the Mediterranean for four months and in the Indian Ocean for the next four months, while the USS Kennedy was in the Mediterranean the entire 8 months. The less aggressive environment of the nuclear powered carrier was compensated for by the highly aggressive environment of the Indian Ocean, compared to that for the USS Kennedy in the Mediterranean.

The results of the corrosion monitoring sensor, installed on the research ship the USNS Vanguard (Fig. 6) during its deployment to the North Sea from March to June 1981, were condensed and plotted as shown in Fig. 9. The plot shows the location of the ship as it cruises from day one. The sensor (probe) output was very high in the Bayonne, NJ, area, which was quite comparable in magnitude to the corrosivity of the environment in the Atlantic and near Southampton, England. The parallel between Bayonne and Southampton was indicative of a commonality that



FIG. 8—Corrosion of Al 7075-T6 alloy step-specimens on an aircraft carrier after (a) four, and (b) eight months exposure.



FIG. 9—Current transients of a copper/steel sensor exposed to a research ship (USNS Vanguard) environment.

both are ports and shipyards. The high sensor readings were expected for these ports, which are semimarine and industrial. This magnitude of corrosivity was equivalent to that of a 5% NaCl salt spray + SO₂ cabinet environment. Slight corrosion activity in the Arctic circle was obviously the effect of rain, fog and, the shipboard environment because of stack gases. There are no aircraft on this ship and, since the Arctic Circle has low temperature and humidity most of the year, very little corrosion activity should be expected.

Environment Simulation Study

The results obtained by the sensor during the shipboard exposure tests indicated large diversities in the environment, where the weather changed frequently from very wet and corrosive to almost normal or calm. It was therefore desirable to examine whether such an environment can be simulated in the laboratory using these data and the sensor. Also, it was questionable whether the corrosivity monitor (sensor) was actually responding to changes in the carrier environment. To determine that, an accelerated cyclic test environment was developed and a copper/steel galvanic sensor was exposed to it. The test environment was comprised of 30 min spray of synthetic sea water followed by a 30 min flow of SO₂ gas at a flow rate of 1 mile/min/ft³ of cabinet volume, and then all activity was stopped for the next two h (the soak period). At the end of the soak period, the cycle starts all over again and continues repeating every three h, up to 120 h. The sensor exposure data obtained from these tests are shown in Fig. 10. As shown in Fig. 10, the current I_g versus exposure time curve is made up of maxima and minima of the corrosion currents, which were consistently repeated after every three h and became very reproducible as the exposure increased in length. The ascending part of the curve coincided with the period when SO₂ gas was flowing into the cabinet after the salt spray had ceased. Thus, the



FIG. 10—A simulated carrier exposure (soak cycle) test demonstrating the sensor sensitivity to environmental changes.

peaks correspond to the point in time where the sensor experienced the highest SO_2 -concentration; i.e., maximum acidity and maximum wetness as the salt fog continues to remain in the chamber for at least 0.5 h after its flow has stopped. The extrapolated dotted lines in the curve (Fig. 10) were drawn to make corrections in the transients during the periods when the cabinet cover was opened for examination, which probably allowed the environment to change and therefore affected the readout. The steady state values of the maxima and minima varied from 50 to 300 μ A, showing extremes of environmental variation.

From the aluminum alloy test-panel exposure testing, it was observed that this synthetic sea salt + SO₂ + soak cycle environment was probably the most corrosive of all accelerated laboratory corrosion testing environments (Table 1) and the type of attack produced had the closest resemblance to that obtained in the carrier environment [8]. Furthermore, the magnitudes of sensor output in this accelerated environment also corresponded with the high output data recorded on the carrier in adverse environments.

Conclusions

The corrosion monitoring sensor is a very usefulness tool in measuring the severity of the environment semiquantitatively. Among the several galvanic systems studied, the copper/steel sensor or probe was most responsive to most varieties of environments in its corrosion sensitivity and reproducibility when used on a continuous basis. In shipboard simulated or accelerated laboratory test environments, the corrosion monitoring ability of the sensor agreed with the cyclic corrosive nature of the environment. The shipboard exposure results indicated that the sensor can provide a realistic corrosion profile of a ship during its mission which, of course, will be specific to the geographical location and season. To develop the corrosion-fingerprints of



FIG. 11—Corrosion severity comparison chart of various environments showing the correlation between the sensor output and the aluminum alloy panel exposure results.

various environments around the world, a number of carriers, conventional and nuclear, must be studied during their missions in all seasons. Effects are being made to install these sensors and test panels and develop a database. A direct correlation between the sensor and the aluminum alloy panel exposure data for a variety of environments was established. This is summarized in the bar chart in Fig. 11, which compares the corrosion severity of these panels with that determined by the sensor. A very high corrosion activity is usually caused by the presence of high wetness, sea salt, SO_2 , and the deposition of particulate matter in the environment, but not necessarily in that order.

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A New Method to Monitor In-Situ Protective Properties of Rust on Weathering Steel

REFERENCE: Ito, S., Kihira, H., and Murata, T., "A New Method to Monitor In-Situ Protective Properties of Rust on Weathering Steel," *Degradation of Metals in the Atmosphere, ASTM STP 965*, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 366-373.

ABSTRACT: To evaluate how protective rust is, and to understand the role rust plays, electrochemical impedance of the rust films on low alloy steels, particularly weathering steels, was studied in a sodium sulfate (Na_2SO_4) solution. By the analysis of the harmonic current, the impedance in the frequency range of 1 Hz to 1.0 kHz is considered to be due to the ion transfer resistance through the rust film, which is dominant factor for the protective properties of the rust films. Based on this principle, a compact instrument was developed to monitor the protective properties of the rust films formed on weathering steels of field structures.

KEY WORDS: monitoring, protective properties, rust, weathering steels, electrochemistry, impedance

Weathering steel containing copper, phosphorus, and so forth has been widely used for bridges, buildings, towers, and other varieties of constructions on account of its excellent corrosion resistance by the protective rust formation resulting from exposure to the atmosphere [1-5]. However, the role of the rust and its formation has not been clarified [6-12]. Moreover, in practice, there has been no quantitative technique for the monitoring of the protective properties of rust films.

Therefore, to evaluate how protective the rust is, and to understand what role the rust plays, the electrochemical impedance of various rusted steels was studied.

Experimental Procedure

The specimens were prepared from various rusted low alloy steels containing weathering steels and conventional carbon steels exposed to a semi-industrial atmosphere over a period of 13 years. In addition, several specimens of weathering steels were artificially rusted in the laboratory to study the effect of rust films on the impedance characteristics. The typical example of chemical composition of test specimens are listed in Table 1.

The electrochemical measurement was made in 0.1 M sodium sulfate (Na₂SO₄) aqueous solution opened to the air, utilizing an AC impedance method [13-17]. The measurement system consists of a computer controlled potentiostat, a frequency response analyzer, and a conventional three compartment glass cell with a saturated Ag-AgCl reference electrode. The amplitude of potential perturbation for impedance measurement and harmonic current measurement were 10 and 80 mV_{rms}, respectively.

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Number	С	Si	Mn	Р	S	Cu	Cr	Ni	v	Ti
27	0.11	0.50	0.40	0.082	0.008	0.40	0.55	0.050		
54	0.09	0.16	1.05	0.025	0.009	0.35	0.45		0.03	0.010
57	0.07	0.35	0.60	0.098	0.012	0.45				0.065
59	0.09	0.35	0.68	0.060	0.050	0.02	0.009	0.004	•••	• • •

TABLE 1-Chemical composition of rusted steel samples for AC impedance measurement.

Results and Discussion

Electrochemical Impedance Measurement of Rusted Steel Exposed to the Atmosphere

The impedance diagram for rusted steels was shown in Fig. 1. Curve a and b represent typical data of rusted weathering steels having protective rust layers beneath the usual rust scale, while Curve c shows that of rusted conventional carbon steel covered with an unprotective rust layer. The characteristics of the curves can be classified into three types of frequency range as summarized in Table 2. Judging from the slope and the phase shift, the impedance in Range A could be supposed to be two ways: Warburg impedance [14] resulting from diffusion phenomena, or the impedance of double layer capacitance at the interface between the rust and steel substrate with



FIG. 1—Typical impedance diagram for electrochemical impedance of various rusted steels exposed to the semi-industrial atmosphere for 13 years.

Range	Frequency	Impedance Characteristics	$\frac{d \log Z}{d \log f}$
A	f < about 1 Hz	pseudo capacitive	$\begin{array}{r} \neq -1 \\ \neq 0 \\ \neq -1 \end{array}$
B	1 Hz $< f < 1.0 kHz$	pseudo resistive	
C	about 1.0 kHz $< f$	pseudo capacitive	

 TABLE 2—Three types of impedance characteristics classified by frequency range.

an indication of dispersion phenomena. Supposed the former case, the impedance in Range B must be charge transfer resistance caused by corrosion reaction connected in series to the Warburg impedance. In order to clarify the causes of the impedance in Ranges A and B, the harmonic currents were measured together with the impedance. The harmonic current usually results from the nonlinear terms of a potential versus current relationship, such as charge transfer reaction represented by the Butler-Volmer equation [13]. The harmonic current spectra of a rusted weathering steel is shown in Fig. 2 together with impedance spectra. If this resistive impedance were the charge transfer resistance, much greater harmonic current should be observed in Range B. Therefore, this resistive impedance can be ascribed to ion migration through the protective rust film. Thus the impedance in Range A is not probable to be Warburg impedance, but the one from the double layer capacitance. In addition, the impedance in Range C can be ascribed to the capacitance of the rust film itself.



FIG. 2—Typical impedance and harmonic current spectra for tightly rusted weathering steel. n = 2 and n = 3 represent the second and the third harmonic current, respectively.

Electrochemical Impedance Measurement of Artificially Rusted Steel

For the purpose of understanding the effect of rust film formation to the impedance spectra and of confirming the cause of the impedance in Range A, the unrusted and rusted steel specimens prepared in the laboratory were investigated by the same method mentioned above.

The obtained results of electrochemical impedance are shown in Fig. 3, where Curve a corresponds to the case of unrusted steel with the surface as polished. This impedance spectra resulted from a typical representation for the simple model of corrosion reaction comprising a charge transfer resistance in the low frequency, a double layer capacitance with a slope 1 in the middle frequency and a solution resistance in the high frequency. Curve b in Fig. 3 shows the data from a specimen whose surface was unevenly covered with rust, while Curve c plots that of a specimen totally covered with rust. The slope of capacitive impedance from double layer obviously deviates from -1 as more corrosion products or rust form on the surface of steel. This phenomenon is well known as dispersion [17], but the reason why dispersion occurs has not been clarified so far. From these results, it is confirmed that the dispersion of impedance is possible to occur when the steel surface is covered by rust, and the capacitive impedance in Range A in Figs. 1 and 2 can be ascribed to the double layer capacitance.

Discussion

Though the various impedance parameters are frequency dependent by the dispersion as rust forms on the steel surface, the impedance data with frequency can be classified into three types of frequency range. The causes of which have been identified, respectively, as follows:



FIG. 3—Changes in impedance characteristics by initial rust formation on steel surfaces.

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- Range A: the double layer capacitance at steel/rust interface C_P .
- Range B: the ion transfer resistance through the rust film R_R .
- Range C: the capacitance of rust itself C_R .

According to this consideration, an equivalent circuit is obtained as depicted in Fig. 4a where R_P denotes the charge transfer resistance caused by corrosion reaction, and R_s denotes the solution resistance. The former can be observed at frequencies lower than 1 mHz. On the contrary, the latter will be in frequencies higher than 100 kHz as shown in Fig. 4b.

New Technique to Monitor Protective Properties of Rust Films

As has been seen in Fig. 1, the difference in electrochemical impedance between the steel with protective rust films (Curves a and b) and the steel with less protective rust film is most distinguishable in frequency Range B. This means that the ion transfer resistance of the rust film R_R ,





FIG. 4—An equivalent circuit for a (a) tightly rusted steel surface and (b) its schematic diagram of impedance.

which represents the barrier against migration of ions, such as Cl^- , SO_4^{2-} , H^+ , OH^- in association with corrosion reaction, is the most dominant factor to assess the protective properties of rust films.

Based on the above principle, a compact instrument was developed to monitor the protective properties of the rust, particularly that on weathering steel. The illustration of the mechanism of this instrument consisting primarily of double probes and the electrical circuitry for impedance measurement is shown in Fig. 5. The electrical circuitry is composed of a current pulse generation (CPG), an electrometer (EM), a phase sensitive detector (PSD), an integrator (INT), an A/D converter (A/D), a central processing unit (CPU), a printer (PRT), and a display (DSP). The alternating current of the most suitable frequency to obtain the ion transfer resistance R_R is applied between the double probes containing Na₂SO₄ solution through the rust films. An excellent correlation between the obtained R_R and the actual corrosion rate of various low alloy steels exposed to a semi-industrial atmosphere for 13 years is shown in Fig. 6. Values of corrosion rates and ion transfer resistances are varied depending on their chemical composi-



FIG. 5-Schematic illustration of measuring system for protective properties of rust films.



FIG. 6—Correlation between rust film resistance R_R and corrosion rate (CR) of various low alloy steels weathered for 13 years in a semi-industrial atmosphere.

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tions. The open circles and solid circles stand for carbon steels and weathering steels, respectively. It is obvious that R_R is the most useful in estimating the protective properties of rust films. This correlation curve may be affected by the environment. Thus, it is necessary to accumulate a data base for various environments.

Conclusions

1. By the analysis of electrochemical impedance with harmonic current for rusted low alloy steels, the impedance in the frequency range of 1 Hz to 1 kHz is considered to be due to the ion transfer resistance, which is the most dominant factor for the protective properties of the rust films.

2. Based on these findings, a compact instrument was developed to monitor the protective properties of the rust films formed on weathering steel structure.

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DISCUSSION

H. E. Townsend¹ (written discussion)—Does your electrochemical impedance spectroscopy method enable you to distinguish between protective and nonprotective rusts formed on weathering steels?

S. Ito, H. Kihira, and T. Murata (authors' closure)-As we reported, the electrochemical impedance measurement gave us a significant information about the protective properties of rust films formed on weathering steels. Through this study, it was found that the ion transfer resistances of rust films, which stand for the barrier against permeation of ions associated with corrosion reaction, are key parameters to distinguish quantitatively between protective and nonprotective rust films on weathering steels. Based on these results, a compact instrument for the field monitoring of the protective properties of rust film was developed.

Okada et al. [1-4] observed the cross sections of rust films using a polarized microscope and characterized that the protective rust film on weathering steel consist of an outer FeOOH layer and an inner dense amorphous rust layer where copper, phosphorus, and other elements are concentrated. The developed instrument exhibits quite high values for the exposure test samples with protective rust films as characterized by Okada et al. Thus, this method is useful to assess the rust films on weathering steels.

It requires the years of exposure for weathering steel to form the protective rust films, and quite complicated reactions occur within the rust films affected by local environmental factors. This period still remains unclarified, and we believe that this instrument will play an important role to clarify the environmental effect on protective rust formation.

Rudolf Schubert¹

A Second Generation Accelerated Atmospheric Corrosion Chamber

REFERENCE: Schubert, R., "A Second Generation Accelerated Atmospheric Corrosion Chamber," Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 374-384.

ABSTRACT: Accelerated atmospheric corrosion testing is an integral part of determining a component's resistance to gaseous attack and is needed to enhance resistance to gaseous attack and subsequent degradation. An acrylic box of 28-L volume with no exposed internal metallic components serves as the basic chamber. All gas lines and fittings are inert. Air with less than 5-ppb total pollutant and a dew point of less than -50° C provides the starting point for air doping. Chamber air is exchanged at a rate of once per minute without a turbulent directed airstream. Chamber temperature is controlled at 30°C and relative humidity (RH) is held at 70%. Current studies utilize 10-ppb hydrogen sulfide (H2S), 10-ppb chloride (Cl2) and 200 ppb nitrogen dioxide (NO2). This environment can be expanded, reduced, or substituted to include other gases such as acid vapors, ozone, and hydrogen peroxide. Pollutant gases are added to the moist make up air at the chamber entrance. All gas flows are controlled through electronic flow meters. National Bureau of Standards (NBS) traceable pollutant standards are regularly scheduled to calibrate monitors. Computer data acquisition of system parameters and control of the electronic flow meters provides for recording and adjustment of system parameters. Spatial pollutant uniformity around the chamber is insured by continuous monitoring of film growth on four copper coated, quartz crystal, thin film monitors. Results of initial data on gold and copper surfaces are presented.

KEY WORDS: accelerated atmospheric corrosion, air pollutants, microbalances, quartz crystal oscillators, water adsorption, copper-chlorine interaction

It has been known for decades [1] that electrical contact performance is degraded because of interactions with nonpure atmospheres. Variables in this interaction can be divided into three general categories, that is, connector characteristics, circuit characteristics, and atmosphere characteristics. Material composition, connection permanency, mechanical wipe, lubrication, and so forth are included in the first group. Voltage, power, impedance, connection frequency, and so forth are listed in the circuit characteristics group. Atmospheric characteristics include dust density, particle size, chemical composition, and concentration. Temperature, relative humidity (RH), and all trace chemical compound concentrations are in the latter group and are the prime items of interest in this paper.

The interaction of atmospheric pollutants and contacts has been studied with a wide variety of metallic alloys, chemical compounds, concentrations, and exposure variables [2-4]. The vast majority of this past work has been done with either single pollutants or concentrations or both at levels much higher than that found in the usual environment; neither case resembles the real environment. Recently the importance of pollutant concentration uniformity throughout the volume, system gas exchange rate, starting pollutant gas levels, multigas interactions, and continuous monitoring of pollutant levels is being recognized [5-8].

This paper describes a second generation accelerated atmospheric corrosion chamber that

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addresses the above parameters and other features. The system includes multigas capability, adjustable pollutant concentration levels near the usual atmospheric concentrations, and less than five part per billion (ppb) pollutant in the source air. In addition, temperature and RH are adjustable, controlled, and monitored (outdoor simulation of dew and sunlight cycles are not included [9]. Continuous system pollutant monitoring is referenced to laboratory standards. Spatial uniformity of pollutant gases, exposure chamber air turbulence, and start-up/termination transients are controlled or monitored. Sample sizes can range from fractions of a centimetre squared (cm^2) surface area for experimental purposes to commercial size printed wiring board assemblies in the 28-L volume. Variable monitoring, selected instrument control, data storage, and data manipulation are performed by a laboratory computer.

System Design Objectives

A universal normal outdoor atmosphere does not exist; wide ranges of atmospheric variables are the rule because of seasonal, geographical, natural, and human influences.² Indoor variations can be greater than or less than the outdoor values depending upon local sources, air handling facilities, building construction, and the pollutant in question [10, 11]. Thus one is forced to choose some arbitrary values and selected pollutant components that are trade-offs to most real conditions and then realize that the components and values chosen are laboratory approximations to natural phenomena [5]. The system design objectives discussed below are listed in Table 1.

All objectives are aimed at enhancing reproducibility from day to day in the same laboratory and between cooperating laboratories. One of the goals of ASTM Committee B-4 on Metallic Materials for Thermostats and for Electrical Resistance, Heating, and Contacts is to set standards for similar systems and tests [12].

Temperature is chosen to be 30° C since this eliminates the variable room temperature setting, which can easily range from approximately 19 to 26° C depending on the laboratory; in addition, 30° C provides an acceleration factor for corrosion in most cases. RH is chosen to be 70% at 30° C, which corresponds to a dew point of 23.9° C. This level is above the value where water vapor concentration is known to enhance corrosion [13-15] and most application levels. Furthermore, it is at a level which most laboratory systems can handle for large air flows without droplets and condensation occurring. To avoid interactions between the system and active gases all components in contact with the active gases are made from fluorinated ethylene polymer (FEP), glass, or polymethyl methacryalate (PMMA). The initial clean air should have the normal concentration of oxygen [16].

TABLE 1-System design objectives.

- 2. Temperature levels at 30°C
- 3. RH at 70% at 30°C
- 4. Sub ppb impurity dry source air
- 5. Multigas, variable concentration impurities
- 6. Gas composition monitoring with calibrated and recorded results
- 7. All inert components in contact with atmosphere
- 8. Minimize sample introduction/removal transients
- 9. Multisized sample introduction ports
- 10. Exhaust gas composition essentially equal to input gas composition
- 11. Uniform, nonturbulent internal atmosphere

²Abbott, W. A., unpublished report.

^{1.} Acceleration factor over normal atmosphere

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Concentrations of pollutant gases should be adjustable around the ASTM trial levels with continuous calibrated monitoring (nitrogen dioxide [NO₂], 200 ppb; hydrogen sulfide [H₂S], 10 ppb; and chloride [Cl₂], 10 ppb). Turbulent air flow in the chamber is undesirable since it is very difficult to create spatially uniform turbulence and correspondingly spatially uniform accelerated corrosion caused by air velocity effects [17]. Exhaust atmosphere composition should essentially be equal to input atmosphere composition so that all sample area is exposed to similar gas concentration, regardless if it is near the gas input or exhaust. Under these trial conditions a film growth rate on copper coupons is expected to be of the order of 10^{-8} gm/cm²/min (175 µg/in.²/(48 h).

To achieve the design criteria of making a standardized accelerated corrosion life test system, the system's volume must be large enough to handle electronic equipment components. These could include printed wiring board assemblies, mechanical relays, and shielded structures, which require large openings for insertion and which would cause concentration variations on start up. Conversely, the system must be able to operate with only small transients for shortterm exposure studies. This requires a range of port sizes designed for smaller samples.

System Design

A system schematic is shown in Fig. 1. An Aadco 737 Pure Air Generator provides 30 L/min of air with a dew point below -50° C (20.8% O₂, balance N₂, argon, carbon dioxide (CO₂), and other inert components) and containing less than 5 ppb of ozone (O₃), sulfur dioxide (SO₂), H₂S, NO_x, carbon monoxide (CO) and hydrocarbons, except methane (CH₄). Matheson electronic flowmeters (EFMs), Model 8250, are used to regulate the ratio of dry air to the amount of



FIG. 1—Schematic illustration of the accelerated atmospheric corrosion chamber showing gas flow paths and computer interactions.

air flowing through a bubbler system to keep the RH at 70%. The humidification system consists of two serial stages of four parallel glass frit bubblers in FEP tanks followed by a glass impact droplet remover. Commercial cylinders of NO₂, Cl₂, and H₂S diluted in zero grade nitrogen to approximately 1000 times the concentration to be used in the experiment are the primary sources of pollutant gases. These gas concentrations are also controlled with EFMs and are combined one at a time with a dry air and then the humid air at the point where the air stream actually enters the corrosion chamber. The pure air streams and humidification system are preheated and maintained at the chamber temperature of 30° C.

All tubing and fittings are FEP, except for the sections that preheat the pure air and are made of OFHC copper. Stopcocks and the droplet remover are glass with glass to FEP tubing joints sealed with FEP "heat shrink" tubing and mechanically protected with polyethylene tubing. The corrosion chamber is constructed of PMMA with no internal exposed metallic hardware. Since the system is at a pressure slightly above atmosphere (needed to move the air around) minor leaks are not of concern. The chamber has a volume of 28 L (30.5 by 30.5 by 30.5 cm) with a 28- by 23-cm gasketed door. Six stoppered holes [7], ranging in size from 0.8 to 1.5 cm, are drilled into the door and designed for rapid insertion of small samples with a minimization of concentration transients [8].

Instrument function, model numbers, and principle of operation are listed in Table 2. The system has been specifically designed without fans. Fans will provide a strong mixing function and generate turbulence, but they are also very directional. This can cause variation in the rate of film growth caused by air stream impacting from one point on a sample surface to another point, since the moving air reduces the normal diffusion length of impurities to the surface. Tompkins [17] has clearly shown that corrosion film growth rate is increased by moving air streams. In the current system, design air is introduced through a perforated FEP tube located on the floor of the chamber and then flows upward into the working area through a perforated FEP sheet. The circle of tubing has 0.8-mm holes every 15 mm on opposite sides. Exhaust gas is removed through a similar perforated tube in the chamber ceiling. To further insure spatial uniformity, the system exhaust gas pollutant concentrations are within 5% of the system input gas concentrations. This is achieved by a high gas turnover rate and limiting the amount of active surfaces present in the chamber at any one time. With the above specified pollutant levels and a 30 L/min input air flow rate the weight of input pollutants is $12 \mu g/min$. This mass flow rate does not include water or oxygen. Preliminary experiments³ have shown that these condi-

Instrument Function	Manufacturer/Model Number	Principle of Operation
Pure air source	Aadco/737	gas chromatography
Pollutant gases	Matheson	premixed with N ₂
Electronic flowmeter	Matheson/8250	variable orifice
Concentration STDs	AIDS	permeation tubes
Temperature control	OMEGA	Type K TC, heating tape
Thin film monitor	L-H Inficon/IC6000	quartz crystal resonance
RH meter	General Eastern/1100DP	dew point
NO _x meter	Monitor Labs/8840	chemiluminescence
H ₂ S meter	Monitor Labs/8770/8850	oxidation/fluorescence
Cl ₂ meter	Mast Development/1724	electrochemical
Instrument control	Digital Equipment Corp.,	RS232C, A to D,
Data recording	PDP 11/23C	D to A, real time

TABLE 2-System components.

³ASTM Committee B-4 on Metallic Materials for Thermostats and for Electrical Resistance, Heating, and Contacts, Task Force on Mixed Gases, personal communication.

tions can produce a film growth rate on copper of the order of $9 \text{ ngm/cm}^2/\text{min}$ including the weight of oxides averaged over 48 h. With up to 65 cm² of reactive surface present less than 5% of the pollutant species are consumed in solid film formation. Thus corrosion uniformity and reproducibility are achieved by using premixed, uniformly moving air and limiting the amount of reactive surface present.

Spatial uniformity of the chamber atmosphere concentration is monitored by having four quartz crystal thin film growth monitors mounted equidistant from the upper corners and each other. The quartz crystals have gold or copper electrodes evaporated onto their faces and resonate at a frequency proportional to their masses including surface film mass. These are controlled by a Leybold-Heraeus Inficon IC6000 monitor. Typical uncalibrated sensitivity is less than a 10 Å change in film thickness (assumed density of 1 g/cm²). Thus spatial uniformity and run to run consistency is immediately and continuously available for inspection.

Pollutant gas monitors (NO₂, H₂S, and Cl₂ meters) are calibrated weekly with zero gas and with permeation tube standards. Tubes are weighed monthly to ensure uniform permeation rates and are exposed to dry air only. Meter zero points are checked with the undoped gas being generated by the Aadco 737 gas source. Values above the desired measurement level are generated by permeation tubes maintained at 30°C. Finally, the commercial cylinder pollutant gases should fall on the zero point/permeation tube point line at the manufacturer's analyzed values. For mixed gas systems one must adjust for interferences, that is, 200-ppb NO₂ causes approximately a 15- to 20-ppb increase in the Cl₂ signal. When these three points are in accord, the pollutant levels are accepted.

Instrument initialization and data recording are done on a DEC 11C23. The actual data taking routine is sufficiently short such that it can be put into the computer system background and other work can be performed in the foreground. Experiments could continue for days at a time giving rise to data volatility concerns. This vulnerability is eliminated by immediately writing the newly recorded data to a hard storage device where it is safe from power transients and can be read out or manipulated at a later time as desired. Table 3 is an outline of the computer programs used to collect data and control the experiments. The data recording program is short enough to run for days in the system background and appears to be transparent to the other operations.

All quartz crystals are ultrasonically cleaned in methanol and then distilled water before use. This cleaning had no noticeable effect on any results. Some of these crystals were cyclically exposed to a 0 to 75% range of RH. A second group of crystals also had 500 nm of copper evaporated on their surface for chlorine exposure at 20 ppb, 0% RH, and 30°C.

TABLE 3—Computer programs and functions.

I.	Initialization program
	(A) initializes instruments
	(B) initializes data storage file space
	(C) records system parameter, comments
П.	Data recording program
	(A) runs in system background
	(B) records specified number of data points at specified frequency
	(C) temporary data display
	(D) permanent data storage
	(E) feedback to wet/dry flowmeter
Ш.	Data analysis programs
	(A) reads files to printer
	(B) options for plotting, manipulating, overlays, and so forth

Results and Discussion

The results of water adsorption and desorption in the PMMA chamber itself is illustrated in Table 4; Column 2 lists the time for the beginning of the measurement series, and Column 7 lists the chamber atmosphere exhaust dew point (DP in °C) at constant temperature for an air flow of 25 L/min. Initial DP is less than or equal to -16° C (DP sensor is only capable of valid readings for DP within a range beginning at 45 C° below the ambient temperature). After Reading 2 (Table 4), some of the dry incoming air was switched to flow through the bubbler system. From Table 4 it is seen that within 2 min the chamber atmosphere is within 95% of its final value.

Hysteresis of drying the chamber is evident in the lower part of Table 4; after Reading 37, the air input was switched to all dry air. It takes over 8 min to reach the 95% dry air level.

The response of four quartz crytal, thin film sensors to changing humidity levels is also shown in Table 4, Columns 3 through 6. Film thicknesses are in angstroms for an assumed film density of unity. Before placing the crystals in the system, they were ultrasonically cleaned in methanol. The results from Sensor 2 versus DP are also shown in graphical form in Fig. 2. One notes that the film thickness continues to increase for 10 min after the atmosphere has reached a steady state value. This is primarily due to the rough cut surface finish of the crystals and will be eliminated when optically smooth crystals are used. Substantial hysteresis on drying is also shown in Fig. 2. An additional 10 min beyond the tabulated values at or below a DP of -15° C is required for the crystals to desorb all their adsorbed water film. These results are in basic agreement with those of King [18] (see Figure 2). Results of Thomas and Sharma [19] on similar crystals indicate a thicker film, but they started adsorption from a vacuum level where their relative zero levels were undoubtly different (Fig. 2). Differences between crystals are not posi-



FIG. 2—Plot of a gold coated quartz crystal adsorbed water film thickness versus system dew point. The data for the figure is taken from Table 4. The line with x points is taken from the paper of Thomas and Sharma [19] while the horizontal bar is a result from King [18].

			Crystal Sen	Dow Point	Tompositure		
Reading	Time	1(Å)	2(Å)	3(Å)	4(Å)	°C	°C
1	15:30:38	0.	0.	0.	0.	-15.9	30.4
2	15:31:11	0.	0.	0.	0.	-16.6	30.6
3	15:31:41	1.	2.	2.	3.	14.3	30.4
4	15:32:14	7.	9.	5.	7.	19.3	30.6
5	15:32:44	14.	18.	9.	13.	22.9	30.6
6	15:33:15	19.	24.	14.	17.	24.2	30.6
7	15:33:45	25.	27.	17.	22.	24.8	30.6
8	15:34:16	30.	30.	20.	25.	25.0	30.6
9	15:34:46	32.	32.	22.	27.	25.1	30.6
10	15:35:17	34.	34.	23.	28.	25.2	30.8
11	15:35:48	34.	36.	24.	30,	25.6	30.8
12	15:36:20	34.	37.	25.	32.	25.6	30.8
13	15:36:54	35.	38.	26.	33.	25.6	30.8
14	15:37:24	35.	39.	27.	33.	25.6	30.9
15	15:37:55	35.	39.	28.	34.	25.8	30.8
16	15:38:27	34.	40.	27.	35.	25.7	30.8
17	15:39: 1	35.	40.	28.	36.	25.4	30.9
18	15:39:33	35.	41.	29.	36.	25.5	30.9
19	15:40: 3	35.	41.	28.	37.	25,6	30.9
20	15:40:37	35.	42.	29.	37.	24.4	30.9
21	15:41: 8	35.	42.	29.	36.	21.2	30.9
22	15:41:40	35.	42.	30.	36.	20,2	30.8
23	15:42:13	35.	42.	30.	36.	23.5	30.9
24	15:42:50	35.	42.	30.	37.	24.3	30.9
25	15:43:21	34.	42.	30.	38.	25.0	30.9
26	15:43:51	35.	43.	31.	39.	26.1	30.9
27	15:44:27	37.	44.	32.	41.	25.7	30.9
28	15:44:56	39.	46.	33.	42.	25.3	30.9
29	15:45:27	41.	46.	33.	45.	25.6	30.9
30	15:45:57	42.	47.	33.	45.	25.6	30.9
31	15:46:31	43.	48.	33.	46.	25.5	30.9
32	15:47: 0	43.	48.	33.	45.	25.5	30.8
33	15:47:31	43.	47.	33.	45.	25.5	30.9
34	15:48: 1	43.	48.	33.	46.	25.5	30.8
35	15:48:35	43.	48.	33.	45.	25.5	30.8
30	15:49: 5	43.	48.	34.	45.	23.3	30.8
3/	15:49:39	43.	48.	34.	45.	25.0	30.9
38	15:50: 9	43.	47.	34.	45.	25.4	30.0
39	15:50:45	42.	47.	34.	44.	25.2	20.8
40	15:51:15	30. 24	34.	24.	22.	22.4	20.8
41	15:51:47	24.	21,	12.	10.	17.7	30.6
42	15.52.17	13.	14.	9. g	13.	17.0	30.0
43	15.52.31	10	12.	0. 9.	13.	11 9	30.0
44	15.53.20	۵. ۱۵	11.	0. 7	12.	2 2	30.0
46	15.54.40	7. 8	10	7.	12.	-92	30.4
47	15:55.19	7	Q.	,. 6	11.	-11 4	30.4
48	15:55:54	6.	9	6.	11.	-13.3	30.2
49	15:56:25	6.	9	6.	10.	-14.3	30.2
50	15:57: 0	5.	8.	5.	10.	-14.9	30.2

 TABLE 4—System response to changes in RH.

	250	H ₂ S	0.9	9.2	13.9	14.9	13.6	13.6	13.6	13.7	13.8	13.2	13.8	14.2	13.1	13.2	13.1	13.9	12.7	13.6	13.7
	ale (ppb) 100	CL_2	02	10	15	18	19	24	29	35	35	37	35	37	36	40	36	37	37	40	39
	% of Full Sc 200	NOx	3.6	53.4	67.0	73.6	77.0	78.3	80.0	80.4	79.8	80.2	81.5	82.3	81.9	81.2	81.2	81.8	82.2	82.7	81.9
	200	ON	1.8	7.9	8.6	6.5	5.7	4.8	4.3	3.9	3.8	3.3	3.6	3.2	3.0	3.2	2.9	2.7	2.7	2.6	2.8
TABLE 5—System parameter with pollutant gases.	Temperature, - °C		29.9	31.4	31.8	30.9	29.9	29.9	31.8	32.0	30.9	29.7	30.2	31.8	32.0	31.1	29.7	29.9	31.8	32.1	31.3
	, A A	Dew Point, °C	-12.1	24.1	24.0	23.1	21.8	21.5	22.5	22.9	22.1	21.2	21.0	22.1	22.8	22.0	20.9	21.0	22.0	22.7	22.1
		4(Å)	o.	20.	25.	23.	17.	12.	19.	27.	24.	18.	13.	20.	28.	25.	19.	13.	20.	30.	28.
	Sensors	3(Å)	ö	16.	22.	21.	18.	15.	20.	27.	26.	21.	18.	24.	31.	30.	25.	21.	26.	35.	34.
	Crystal S	2(Å)	0	31.	40.	42.	37.	34.	41.	50.	46.	40.	37.	46.	53.	49.	43.	40.	46.	55.	53.
		1(Å)	ō	34.	41.	38.	31.	28.	37.	46.	43.	38.	34.	44.	53.	51.	45.	41.	50.	61.	60.
		Time	16:59:13	17:15:49	17:32:22	17:48:52	18: 5:22	18:21:55	18:38:25	18:55: 3	19:11:44	19:28:15	19:44:50	20: 1:24	20:17:58	20:34:35	20:51: 4	21: 7:34	21:24: 5	21:40:38	21:57:11
		Reading	-	2	ę	4	S	9	7	œ	6	10	11	12	13	14	15	16	17	18	19

00	
pollutant	
with	
parameter	
-System	

tion dependent, but rather crystal sensor dependent. For example, if one interchanges only Crystal 2 and Crystal 3 in their sensor holders and repeats the experiment, data in Columns 4 and 5 (Table 4) are transposed.

Table 5 illustrates the system's stability with pollutant gases. The first 8 columns are similar to Table 4; film thicknesses are seen to be comparable to that formed with water vapor alone. This is not surprising since the metallic electrodes of the quartz cystals are evaporated gold, which is not readily attacked by the pollutant gases. Columns 9 and 10 are percent of full scale for NO and NO_x where NO_x represents NO + NO₂. The values for NO after a 3-h warm up are near the instrument zero with a small contribution from the chamber atmosphere. NO_x levels show a stability of $\pm 2\%$ of full scale over the experimental time period. Column 12, the H₂S level, also runs very stable at $\pm 2\%$ of full scale. The chlorine reading in Column 11 is variable over the experimental time frame at these concentration levels; its variability is typically $\pm 25\%$ of full scale. This parameter needs substantially more laboratory effort to improve the detection



FIG. 3—Plot of weight gain versus exposure time for quartz crystal sensor with a 500-nm evaporated copper film on one surface. Atmosphere is clean, dry air doped with 20 ppb of chlorine gas. The range of values are primarily caused by the surface roughness of the cut crystals.

electronics, which are operating near their limits of usefulness. Repeated experiments over larger periods of time with permeation tubes as the gas source have yielded similar results.

Copper evaporated on quartz crystals has been exposed to dry chlorine gas at 20 ppb for 30 h. The weight gain per square cm versus time is shown in Fig. 3. The range of values shown is attributable primarily to surface roughness; different crystals will have differing amounts of copper available for reaction per cm². The average value for the 30-h period is approximately $0.06 \ \mu g/cm^2h$. This is in good agreement with the data of Rice et al. [6] if one extrapolates their data to the zero humidity case.

Conclusions

A second generation accelerated atmospheric corrosion chamber has been assembled and demonstrated. Features include temperature, relative humidity, NO₂, Cl₂, and H₂S, adjustability, control, and level recording. System spatial uniformity and low turbulence air flow are verified by multiple quartz crystal thin film monitors. System atmosphere exchange rates of once per minute allows up to 65 cm^2 of active surface area to be exposed at one time without depleting pollutant levels. Fractional cm² sized samples to industrial sized samples can readily be accommodated in the 28-L volume with start-up transients ranging from seconds to 2 min depending on sample size. Continuous data recording and system control can be performed over periods of days by laboratory computer. Equipment from a variety of manufacturers has been satisfactorily integrated. The system has been tested by adsorption and desorption of water films on evaporated gold films and the adsorption of water and pollutant films on evaporated gold films. Preliminary results of 20-ppb Cl₂ exposure to copper in dry air shows agreement with the results of others. Reasons for the variability in the indicated chlorine level versus time remains to be determined.

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ISO CORRAG Collaborative Atmospheric Exposure Program: A Preliminary Report

REFERENCE: Dean, S. W., **"ISO CORRAG Collaborative Atmospheric Exposure Program: A Preliminary Report,"** Degradation of Metals in the Atmosphere, ASTM STP 965, S. W. Dean and T. S. Lee, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 385-431.

ABSTRACT: This report summarizes the U.S. TAG effort to participate in the International Standards Organization Technical Committee (ISO/TC) 156 WG4 worldwide atmospheric exposure program. This program is being sponsored by ASTM Subcommittee G01.04 on Atmospheric Corrosion. This report lists the individuals responsible for supplying materials for this program and it identifies the individuals responsible for site exposures and withdrawals. It also provides specifications for the panel identifications, data sheets, and specimen exposure reports. Some of the initial data on panels in the program as well as the ISO report on the program are given in the appendices to this report.

KEY WORDS: atmospheric corrosion, standards, atmospheric exposure, aluminum, zinc, copper, steels

Introduction

The International Standards Organization Technical Committee 156 (ISO/TC 156) on Corrosion of Metals and Alloys is responsible for writing standards concerning corrosion testing and corrosion resistance within the ISO. One aspect of this work has been the classification of atmospheric corrosivity on a worldwide basis. It has long been recognized that outdoor atmospheric exposures varied greatly in corrosivity with respect to materials of construction. Furthermore, it is well known that interior exposures are generally much less corrosive than outdoor exposures. As a result, designers and engineers have needed a system to categorize the corrosivity of the atmosphere so that appropriate protective measures could be specified.

Working Group 4 of ISO/TC 156, under the leadership of Czechoslovakia, is responsible for determining a classification system for atmospheric corrosivity. The system currently being considered is based on two approaches. The characteristics of the atmosphere in question may be measured or estimated and its corrosivity may be inferred from this information. A second approach is to expose standard panels and determine the corrosion damage after a period of time. However, it is essential to this system that the corrosivity estimated by the first approach agree with the results obtained from the second. In order to verify that the proposed approach for estimating corrosivity is valid, an exposure program has been formulated using four different metals: steel, copper, aluminum, and zinc. This exposure program is to be carried out simulta-

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neously throughout the world by member bodies of ISO/TC 156. This program has been given the name ISO CORRAG.

The U.S. participation in ISO CORRAG has been handled by ASTM Technical Committee G-1 on the Corrosion of Metals. Standing Committee G01.95, the Technical Advisory Group to ISO/TC 156, and Subcommittee G01.04 on Atmospheric Corrosion have provided support to carry out this program. Consequently, any question or comment on the ISO CORRAG program should be addressed to ASTM Committee G-1. This preliminary report includes the numbering system and a list of individuals responsible for the various panels, exposure sites, and reports. The ISO report on this program, which is appended to this paper, provides preparation procedures, exposure plans, and nations participating in the program. Both of these documents are reprinted in this STP as a permanent record of the exposure program.

1. Specimen Suppliers and Evaluators

The materials used for this program are being supplied by a number of companies that have made the U.S. participation in this program possible through their generosity. The steel and zinc panels will be partially prepared and evaluated by laboratories not associated with the producer.

1.1 Aluminum panels

The aluminum panels will be supplied and evaluated by Kaiser Aluminum and Chemical Corporation. Contact:

Mr. Thomas J. Summerson Kaiser Aluminum and Chemical Corporation Center for Technology Box 877-6177 Sunol Blvd. Pleasanton, CA 94566 415/462-1122

1.2 Copper Panels

The copper panels will be supplied and evaluated by Olin Corporation, Metals Research Laboratories. Contact:

Dr. Ned W. Polan Olin Corporation Metals Research Laboratories 91 Shelton Avenue New Haven, CT 06511 203/789-5292

1.3 Zinc Panels (Alloy 220, 0.8% Cu, 0.12% Ti)

Supplier: Platt Bros. Contact:

Mr. John Koenig Platt Bros. P.O. Box 1030 Waterbury, CT 06721 203/753-4194 Evaluator: Air Products & Chemicals, Inc. Contact:

Dr. Sheldon W. Dean Air Products & Chemicals, Inc. P.O. Box 538 Allentown, PA 18105 215/481-7476

1.4 Steel Panels

Supplier: British Steel Corporation Contact:

Mr. B. V. Lee British Steel Corporation Swinden Laboratories Moorgate, Rotherkane, S60 3AR United Kingdom Telephone: 0709 60166 Telex: 547279 Evaluator: Cortest Laboratories Contact:

Dr. Russell D. Kane Cortest Laboratories, Inc. Suite 102 11115 Mills Road Cypress, TX 77429 713/890-7575

1.5 Helix Wire Specimens

Supplier: DIN Contact:

> Dr. Carl L. Kruse Staatliches Materialprüfungsamt NW Marsbruchstrasse 186 D-4600 Dortmund 41 West Germany (Federal Republic of Germany)

2. Site Information

2.1 Kure Beach-250 m lot (East Coast Marine)

Contact:

Dr. W. W. Kirk LaQue Center for Corrosion Technology, Inc. P.O. Box 656 Wrightsville Beach, NC 28480 919/256-2271 Alternate:

Mr. Earl Baker LaQue Center for Corrosion Technology, Inc. P.O. Box 656 Wrightsville Beach, NC 28480 919/256-2271

2.2 Newark Kearney (Industrial)

Contact:

Mr. Victor Chaker Port Authority of New York and New Jersey Technical Center, Room 231 241 Erie Street Jersey City, NJ 07302 201/963-2942

2.3 Point Reyes (West Coast Marine)

Contact:

Mr. Thomas J. Summerson Kaiser Aluminum and Chemical Corporation Center for Technology Box 877-6177 Sunol Blvd. Pleasanton, CA 94566 415/462-1122

Alternate:

Mr. Harry N. Alderson Pacific Gas and Electric Company Dept. of Engineering Research 3400 Crow Canyon Road San Ramon, CA 94583 415/820-2000

2.4 Research Triangle Park (Rural)

Contact:

Dr. Edward Edney Mail Drop 8 Environmental Protection Agency Environmental Research Center Research Triangle Park, NC 27711

Alternate:

Mr. John Spence US EPA ASRL Mail Drop Research Triangle Park, NC 27711 919/541-2649

2.5 Panama Canal Zone (Tropical)

Contact:

Ms. Kathleen Bamberg Materials Technology Laboratory Arsenal Station Attn: SLCMT-MRS-ES Watertown, MA 02172-0001 617/923-5564

Alternate:

Mr. George F. Downs III Commander, U.S. Army Tropic Test Center Attention: ST ETC-MTD-S (Downs) P.O. Drawer 942 APO Miami 34004 Phone: 011-507-85-4256

2.6 Los Angeles (West Coast Urban)

Contact:

Prof. Florian Mansfeld University of Southern California Dept. of Materials Science VHE 714 Los Angeles, CA 98089-0241 213/743-6424

3. Specimen Number Requirements

3.1 Material supplier requirements: 9 exposures \times 3 panels per exposure \times 6 sites = 162 panels + 18 spares = 180 panels total.

3.2 Site requirements

3.2.1 Panels: 9 exposures \times 3 replicates per exposure \times 4 materials = 108 panels + 12 spares = 120 panels on hand.

3.2.1.1 Panels initially exposed (Oct. 1986 target): 4 exposures (1 year, 2 year, 4 year, \times year) \times 3 replicates \times 4 materials = 48 panels.

3.2.1.2 Panels exposed (April 1987): 1 exposure \times 3 replicates \times 4 materials = 12 panels; total on exposure = 60 panels.

3.2.1.3 Panels exposed (Oct. 1987) = 12 panels. Panels removed (Oct. 1987) = 12 panels. Spaces occupied = 60.

3.2.2 Helix specimens

3.2.2.1 9 exposures \times 3 replicates \times 4 materials = 108 helix specimens on hand.

3.2.2.2 Helix specimens exposed—see 3.2.1.1 through 3.2.1.3 above.

4. Specimen Identification System

4.1 Nonferrous Metal Panels

4.1.1 Stamp identification code on each panel with steel stencil stamp 1/8 by 1/4 in. character size.

4.1.2 Location of identification marks: See Fig. 1 for sample. All identification marks to be made on the top surface, lower left hand corner of panel as mounted in rack. Stencil marks to be at least 0.5 in. from either edge.

4.1.3 Identification system: the following markings should be placed on each panel: program identification, materials number, site letter, exposure numbers, specimen number and specimen type.

- Program identification letter: I.
- Material numbers:
 - 1 = aluminum,
 - 2 = copper,
 - 3 = zinc, and
 - 4 = steel.

NOTE: Steel panels use a different system. This number is used for reference and will be useful for helical specimens.



FIG. 1-ISO CORRAG nonferrous panel identification plan.
• Site letters:

A = Kure Beach, B = Newark Kearney, C = Point Reyes, D = Research Triangle Park, E = Panama Canal Zone, andF = Los Angeles.

• Exposure numbers: Two digits will be used to designate the exposure. The first digit indicates the exposure duration in years; the second indicates the time when exposure was initiated:

1 = Winter 1987, 2 = Spring 1987, 3 = Fall 1987, 4 = Spring 1988, 5 = Fall 1988, 6 = Spring 1989, and 7 = extra panel.

- Panel number: sequential 1-3.
- Specimen type: P = panel and H = helix.

An example is as follows:

First zinc panel, 2-year exposure at Newark Kearney: I3B211P (Fig. 1)

4.2 Steel panel: Use four 1/8 in. drilled holes to identify panels. See Fig. 2 for detailed layout of holes.

4.3 Wire helix specimens: The same identification system will be used for wire helix specimens, except that the final mark will be "H" rather than "P."

5. Material Supplier Report

Each material supplier should provide the following information:

- 5.1 Chemical analysis of alloy supplied.
- 5.2 Unified Numbering System (UNS) and ASTM designation of material supplied.
- 5.3 Mechanical properties, if available.
- 5.4 Date of shipment.
- 5.5 Remarks, including lot identification of material, if available, and temper supplied.

6. Specimen Preparation Report

6.1 Each laboratory providing specimens ready for exposure should provide data sheets with the mass, size, and identification for each panel; See Fig. 3.

6.2 The evaluator should also provide a report detailing the cleaning procedure, packaging, and shipment dates.

7. Exposure Reports

Each site contact should report the date, time, weather information, and location of each panel exposed. See sample specimen exposure report form (Fig. 4).



Designation to be accomplished by drilling four $1/8" \phi$ holes in the appropriate location.

FIG. 2-ISO CORRAG steel panel identification plan.

8. Report Distribution

All reports described in Sections 4 through 6 above should be distributed to the following:

- Chairman of Committee G-1 Mr. Harvey Hack Naval Ship R&D Center Code 2813 Annapolis, MD 21402 301/267-3502
- Staff Manager of Committee G-1 Beth Kilburn ASTM 1916 Race St. Philadelphia, PA 19103 215/299-5517

ISO CORRAG PROGRAM

DATA SHEET

Material: Steel Panels Exposed at Kure Beach

Code	Original Mass	Final Mass	Ma <u>ss Loss</u>	Dimensions L W T	Date Exposed	Date Removed
I 44111P						
I 4A112P						
I 4A113P						
I 4A121P						
I 4A122P						
I 4A123P						
I 4A131P						
I 4A132P						
I 4A133P						
I 4A141P						
I 4A142P						
I 4A143P						
I 4A151P						
I 4A152P						
I 4A153P						
I 4A161P						
I 4A162P						
I 4A163P						
1 4A211P						
1 4A212P						
I 4A213P						
I 4A411P						
I 4A412P						
I 4A413P						
I 4AX11P						
I 4AX12P						
I 4AX13P						
Engineer Respo	onsible for Speci	men Preparati	on:			
Date:						

FIG. 3-Sample data sheet.

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ISO CORRAG PROGRAM

SPECIMEN EXPOSURE REPORT

Site:					
Date of A	Action:		Time:		
Weather a	at Site - Temperatur	e:	S	iky:	
	Wind Speed	& Direction:		Precipitation:	
Engineer	Responsible for Exp	oosure:			
	Specimens Exposed				
<u>Code</u>	Rack	<u>Stand</u>	<u>Code</u>	<u>Rack</u>	<u>Stand</u>

FIG. 4-Sample specimen exposure report form.

- Chairman, Subcommittee G01.04 Dr. W. W. Kirk LaQue Center for Corrosion Technology, Inc. P.O. Box 656 Wrightsville Beach, NC 28480 919/256-2271
- Chairman, Standing Committee G01.95 Dr. Sheldon W. Dean Air Products & Chemicals, Inc. P.O. Box 538 Allentown, PA 18105 215/481-7476
- U.S. Representative to ISO/TC 156/WG4 Dr. Robert Baboian Texas Instruments, Inc. Mail Station 10/13 34 Forest St. Attleboro, MA 02703 617/699-1350

9. Other Information on the ISO CORRAG Program

Some initial data on panels in the program and Report ISO/TC 156/WG4/N131 follow as appendices to this paper.

APPENDIX A

Supplier Information on Steel Specimen Material

Supplier: British Steel Corporation Swinden Laboratories Moorgate Rotherham, S60 3AR Contact: B. V. Lee

Both panels and wire of the same lot. Panels: 1 mm thickness. See Table A1 for chemical analysis.

Component	Mass Percent
С	0.056
Si	0.060
S	0.012
Р	0.013
Cr	0.02
Ni	0.04
Cu	0.03
Al	0.02
N	0.004
Mo, Nb, Ti, V, Sn	0.01

TABLE A1—Chemical analysis, mass percent.

APPENDIX B

Supplier Information on Zinc Panel Material

Supplier: The Platt Bros. & Co. P.O. Box 1030 Waterbury, CT 06721 Contact: John J. Koenig

Designation: Platt #220 Zinc Alloy Lot identification: M0408 Nominal tensile strength: 207 MPa (30 000 psi) See Table B1 for chemical analysis.

TABLE	B1—Chemical analysis,
	mass percent.

Components	Mass Percent
Pb	0.006 max
Fe	0.001 max
Cd	0.005 max
Cu	0.5 to 0.7
Ti	0.12 to 0.16
Zn	balance

TABLE	C1-Zinc panels ex	posed at Kure	Beach.	TABLE C	2—Zinc panels expo	osed at Newark	Kearney.
Panel ID	Initial Mass, g	Length, in.	Width, in.	Panel ID	Initial Mass, g	Length, in.	Width, in.
13A111P	113.68065	6.01	4.00	13B111P	115.607960	6.03	4.00
13A112P	113.75143	5.99	4.00	I3B112P	113.875090	6.00	4.00
13A113P	113.60266	6.01	4.00	13B113P	114.873150	6.01	4.00
I3A211P	113.80755	6.00	4.00	13B211P	114.042990	5.99	4.00
13A212P	113.60570	6.00	4.00	[3B212P	114.544510	6.02	4.00
13A213P	113.56118	6.00	4.00	I3B213P	113.814076	6.01	4.00
I3A411P	113.65630	6.00	4.00	I3B411P	113.603870	6.00	4.00
13A412P	114.36291	6.00	4.00	13B412P	114.517880	6.00	4.00
13A413P	114.95432	6.02	4.00	13B413P	114.925930	6.01	4.00
13AX11P	115.61388	6.01	4.00	13BX11P	114.153080	6.00	4.00
13AX12P	115.23407	6.01	4.00	13BX12P	113.130130	6.00	4.00
13AX13P	114.69842	6.00	4.00	13BX13P	113.655140	6.00	4.00
13A121P	114.50821	6.01	4.00	13B121P	113.696710	6.00	4.00
I3A122P	114.26026	6.00	4.00	13B122P	114.481180	6.01	4.00
13A123P	114.12737	6.01	4.00	I3B123P	114.557730	6.02	4.00
13A131P	114.67838	5.99	4.00	I3B131P	114.484740	6.01	4.00
13A132P	114.62444	6.00	4.00	13B132P	114.598980	6.02	4.00
13A133P	114.24130	6.00	4.00	I3B133P	114.313890	6.00	4.00
13A141P	114.34976	6.00	4.00	I3B141P	114.742090	5.99	4.00
13A142P	114.58515	6.00	4.00	I3B142P	115.435750	6.00	4.00
13A143P	115.01093	6.02	4.00	[3B143P	115.814030	6.02	4.00
13A151P	114.61207	6.01	4.00	[3B151P	114.157590	6.00	4.00
13A152P	114.56684	6.01	4.00	13B152P	114.246800	6.01	4.00
13A153P	114.91257	6.02	4.00	I3B153P	114.664920	6.01	4.00
I3A161P	113.78670	6.01	4.00	13B161P	114.661970	6.01	4.00
I3A162P	112.90572	5.98	4.00	13B162P	114.653380	6.01	4.00
I3A163P	113.75268	6.02	4.00	13B163P	114.094730	6.00	4.00
I3A171P	113.93600	6.02	4.00	13B171P	113.654590	6.01	4.00
I3A172P	114.04235	6.00	4.00	13B172P	113.477090	6.00	4.00
I3A173P	114.77735	6.01	4.00	I3B173P	113.268450	5.99	4.00
Note: Thicl	kness of all panels =	= 0.04 in.		Nore: Thich	<pre>cness of all panels =</pre>	= 0.04 in.	

Tables C1 through C6 contain data for each site where zinc panels were exposed.

APPENDIX C

TABLE C4-	Zinc panels exposed	l at Research T	riangle Park.
Panel ID	Initial Mass, g	Length, in.	Width, in.
[3D111P	114.07537	6.02	4.00
I3D112P	113.21380	6.00	4.00
13D113P	113.82506	6.02	4.00
13D211P	113.09957	6.00	4.00
I3D212P	113.19787	5.98	4.00
I3D213P	115.89675	6.08	4.00
I3D411P	113.95395	6.00	4.00
I3D412P	114.37486	6.08	4.00
I3D413P	114.71070	6.02	4.00
13DX11P	115.73464	6.11	4.00
I3DX12P	114.26254	6.00	4.00
13DX13P	115.08773	6.01	4.00
I3D121P	114.43426	6.00	4.00
I3D122P	113.83429	6.01	4.00
I3D123P	115.75326	6.09	4.00
[3D131P	114.26387	6.02	4.00
I3D132P	115.98569	6.11	4.00
I3D133P	115.77339	6.11	4.00
I3D141P	113.42840	6.00	4.00
I3D142P	113.76153	6.03	4.00
I3D143P	113.85063	6.01	4.00
13D151P	113.79730	6.01	4.00
I3D152P	113.27938	5.99	4.00
I3D153P	113.50382	6.00	4.00
I3D161P	114.51695	6.00	4.00
13D162P	114.17347	6.02	4.00
I3D163P	113.81255	6.00	4.00
I3D171P	114.02626	6.01	4.00
13D172P	114.07049	6.01	4.00
13D173P	113.76678	6.00	4.00
Note: Thicl	kness of all panels =	= 0.04 in.	
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	co-zinc panels es	cposed at Foint	Keyes.
Panel ID	Initial Mass, g	Length, in.	Width, in.
13C111P	114.30629	5.99	4.00
I3C112P	115.54545	6.03	4.00
13C113P	114.41745	6.00	4.00
13C211P	114.56360	6.00	4.00
13C212P	114.59252	6.00	4.00
I3C213P	114.58860	6.01	4.00
I3C411P	114.35194	6.02	4.00
I3C412P	114.58637	6.00	4.00
I3C413P	114.20851	6.01	4.00
IJCX11P	113.80160	6.01	4.00
13CX12P	114.34600	6.01	4.00
13CX13P	112.82900	5.99	4.00
I3C121P	113.77717	6.01	4.00
13C122P	113.47472	6.00	4.00
13C123P	113.25854	6.00	4.00
I3C131P	113.95860	6.01	4.00
13C132P	114.98791	6.10	4.00
13C133P	114.84607	6.10	4.00
I3C141P	114,14842	6.05	4.00
I3C142P	114.30437	6.08	4.00
13C143P	113.97399	6.05	4.00
13C151P	114.28563	6.04	4.00
13C152P	113.70788	5.99	4.00
13C153P	112.77015	6.00	4.00
13C161P	112.60906	5.97	4.00
13C162P	113.69698	6.01	4.00
13C163P	113.24193	5.99	4.00
13C171P	114.26155	6.01	4.00
I3C172P	114.29740	6.00	4.00
I3C173P	115.05338	6.02	4.00
Note: Thick	ness of all panels =	= 0.04 in.	

DEAN ON THE ATMOSPHERIC EXPOSURE PROGRAM 397

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-Zinc panels exposed	Initial Mass, g Leng	113.60700 6	113.81535 6	113.58483 6	113.98618 6	113.46596 6	112.66919 5	113.56424 6	113.32882 6	113.35676 5	113.95122 6	113.49905 6	113.40760 6	113.21615 6	113.73699 6	113.48965 6	113.85985 6	114.09682 6	113.62998 6	113.58123 6	113.65753 6	114.17767 6	113.60935 5	113.79344 6	113.38519 5	114.80033 6	114.72368 6	114.18759 6	113.81601 6	113.66756 6	114.02045 6	
TABLE C6	Panel ID	I3F111P	13F112P	13F113P	I3F211P	13F212P	I3F213P	I3F411P	13F412P	I3F413P	13FX11P	13FX12P	13FX13P	13F121P	I3F122P	I3F123P	I3F131P	13F132P	I3F133P	I3F141P	I3F142P	I3F143P	13F151P	I3F152P	13F153P	13F161P	13F162P	13F163P	I3F171P	13F172P	I3F173P	

TABLE C5-	-Zinc panels expose	ed at Panama (Canal Zone.
Panel ID	Initial Mass, g	Length, in.	Width, in.
I3E111P	114.17546	6.01	4.00
I3E112P	112.97065	5.98	4.00
13E113P	114.03899	6.00	4.00
I3E211P	114.60718	6.02	4.00
13E212P	113.89165	6.02	4.00
13E213P	114.09123	6.00	4.00
I3E411P	113.72576	5.99	4.00
I3E412P	114.15693	6.00	4.00
I3E413P	114.31129	6.01	4.00
13EX11P	113.57576	6.01	4.00
I3EX12P	113.15143	6.00	4.00
13EX13P	114.58006	6.02	4.00
I3E121P	114.52255	6.01	4.00
13E122P	113.56140	6.00	4.00
I3E123P	113.59297	6.01	4.00
I3E131P	113.70864	6.01	4.00
I3E132P	114.59897	6.02	4.00
I3E133P	113.62737	6.00	4.00
I3E141P	114.56668	6.02	4.00
I3E142P	114.66717	6.01	4.00
I3E143P	113.73651	6.00	4.00
I3E151P	113.71654	6.00	4.00
13E152P	114.24565	6.02	4.00
13E153P	114.06888	6.01	4.00
I3E161P	113.95880	6.00	4.00
I3E162P	114.15056	6.02	4.00
I3E163P	113.82869	6.01	4.00
I3E171P	114.55856	5.99	4.00
13E172P	114.43186	6.01	4.00
I3E173P	113.69380	6.00	4.00
Note: Thich	cness of all panels =	= 0.04 in.	

nitial Mass, g 106.094 105.853						
106.094 105.853	Length, in.	Width, in.	Panel ID	Initial Mass, g	Length, in.	Width, in.
105.853	6.012	4.012	I2B111P	106.257	6.006	4.035
105 050	6.007	4.012	I2B112P	106.262	6.009	4.039
UCK.CUI	6.001	4.011	I2B113P	107.347	6.029	4.045
106.261	6.005	4.020	12B121P	106.834	6.021	4.042
106.504	6.010	4.025	I2B122P	105.936	6.010	4.045
107.120	6.007	4.030	I2B123P	105.790	6.006	4.044
104.998	6.026	4.009	I2B131P	106.244	6.019	4.040
106.722	6.006	4.041	I2B132P	106.733	6.020	4.039
106.775	6.002	4.040	I2B133P	107.074	6.008	4.040
105.729	6.012	4.038	I2B141P	107.670	6.006	4.042
106.567	6.014	4.040	I2B142P	106.754	6.003	4.048
106.017	6.020	4.039	I2B143P	105.896	6.030	4.010
105.875	6.029	4.035	I2B151P	105.867	6.036	4.007
107.737	6.006	4.042	I2B152P	107.003	6.010	4.045
107.193	6.005	4.036	I2B153P	107.072	6.003	4.041
107.514	600.9	4.039	I2B161P	106.679	6.005	4.040
105.636	6.002	4.008	I2B162P	106.791	6.004	4.036
106.509	6.005	4.009	I2B163P	104.138	5.977	4.004
106.451	6.010	4.035	I2B211P	105.202	6.020	4.003
106.207	6.008	4.031	I2B212P	105.106	6.013	4.006
106.953	6.005	4.033	I2B213P	104.776	6.006	4.006
105.333	6.007	4.005	I2B411P	104.415	6.005	4.005
105.122	6.013	4.004	I2B412P	104.960	6.017	4.004
105.158	6.006	4.007	I2B413P	104.922	6.025	4.005
105.727	6.006	4.014	I2BX11P	105.020	5.988	4.004
105.205	6.010	4.013	I2BX12P	105.084	5.976	4.009
104.581	6.006	4.007	12BX13P	105.337	6.018	4.006
105.844	5.981	4.035	I2B 71P	105.767	6.019	4.018
104.228	5.993	4.005	12B 72P	106.003	6.001	4.042
103.631	5.926	4.027	I2B 73P	105.890	5.994	4.043

Tables D1 through D6 contain data for each site where C/10 copper panels were exposed.

APPENDIX D

Researc	
at	
exposed	
panels	In Daub
copper	Triano
-C110	
E D4-	

4—C110 copper panels exposed at Research Triangle Park.	Initial Mass, g Length, in. Width, in.	104.982 6.013 4.004	104.763 6.012 4.001	104.847 6.017 4.002	104.943 6.013 4.003	105.160 6.025 4.005	104.753 6.015 4.007	103.807 5.930 4.004	104.251 5.944 4.006	104.445 5.960 4.003	104.803 5.977 4.009	105.538 6.045 4.006	105.201 6.036 4.003	104.942 6.036 4.003	105.827 6.002 4.010	106.434 6.005 4.006	105.766 6.011 4.007	105.456 6.001 4.009	105.051 6.016 4.005	105.335 5.964 4.020	105.550 6.021 4.024	105.710 6.021 4.021	106.443 6.028 4.006	106.238 6.018 4.005	106.015 6.025 4.010	106.034 6.024 4.005	106.364 6.005 4.024	106.913 6.006 4.024	104.845 6.011 4.003	
TABLE D4C110 cop Tr	Panel ID Initial Ma	12D111P 104 95	I2D112P 104.76	I2D113P 104.84	I2D121P 104.94	I2D122P 105.16	I2D123P 104.75	I2D131P 103.8(I2D132P 104.25	I2D133P 104.44	I2D141P 104.80	I2D142P 105.53	I2D143P 105.20	I2D151P 104.94	I2D152P 105.82	I2D153P 106.43	I2D161P 105.76	I2D162P 105.45	I2D163P 105.05	I2D211P 105.33	I2D212P 105.55	I2D213P 105.71	I2D411P 106.4	I2D412P 106.23	I2D413P 106.01	I2DX11P 106.03	I2DX12P 106.36	I2DX13P 106.91	12D 71P 104.84	

anel ID Initial Mass, g Length, in. Wi 2C111P 105.304 5.996 0.035 2C112P 105.314 5.996 6.033 2C121P 105.3189 6.029 6.033 2C121P 105.368 6.025 6.033 2C121P 105.368 6.025 6.033 2C131P 105.970 6.031 6.025 2C131P 105.970 6.014 6.024 2C141P 105.191 6.025 6.024 2C141P 105.191 6.024 6.014 2C141P 105.191 6.024 6.024 2C151P 104.775 6.012 6.024 2C141P 105.175 6.006 6.003 2C151P 106.778 6.026 6.001 2C151P 105.604 6.001 6.002 2C151P 105.5175 6.002 6.010 2C151P 106.778 6.002 6.001 2C151P 106.558 6.001 <td< th=""><th>ABLE D3-</th><th>-CIIU copper pane</th><th>ls exposed at P</th><th>oint Reyes.</th></td<>	ABLE D3-	-CIIU copper pane	ls exposed at P	oint Reyes.
1111 105.304 5.996 1112P 105.304 5.996 1121P 105.304 5.996 1121P 105.304 5.996 1123P 105.308 6.033 1123P 105.308 6.031 1123P 105.308 6.031 1123P 105.308 6.031 1131P 105.308 6.031 1131P 105.308 6.031 1141P 105.3145 6.026 1151P 104.775 6.024 1151P 105.145 6.024 1151P 105.530 6.024 1152P 105.530 6.005 1153P 105.540 6.003 1151P 105.560 6.003 1152P 105.560 6.003 1152P 105.573 6.002 1152P 105.560 6.003 1152P 105.573 6.001 1152P 105.573 6.001 1152P 105.670 6.001 1152P 105.674 6.001 <td< th=""><th>el ID</th><th>Initial Mass, g</th><th>Length, in.</th><th>Width, in.</th></td<>	el ID	Initial Mass, g	Length, in.	Width, in.
1112P 105.237 6.035 1121P 105.368 6.033 1121P 105.368 6.025 1132P 106.029 6.025 1131P 105.145 6.024 1141P 105.145 6.024 1141P 105.145 6.024 1151P 105.778 6.024 1521P 105.778 6.003 1521P 105.670 6.003 1521P 105.670 6.003 1521P 105.775 6.003 165.690 6.003 6.001 155.690 6.003 6.001 155.691 105.775 6.003 1632 105.690 6.001 111P 105.690 6.001 112P 105.690 6.001 113P 105.690 6.001 1141P 105.690 6.001 1	111P	105.304	5.996	4.031
113P 105.189 6.029 122P 105.368 6.023 123P 105.370 6.031 133P 105.370 6.031 133P 106.079 6.031 133P 106.079 6.031 133P 106.079 6.031 133P 104.967 6.014 141P 105.145 6.026 151P 105.145 6.024 151P 105.773 6.026 152P 105.778 6.003 152P 105.778 6.003 161P 105.604 6.003 152P 105.678 6.003 153P 105.678 6.003 153P 105.775 6.003 165.690 6.003 6.001 211P 105.690 6.003 165.775 6.006 6.001 211P 105.606 6.001 211P 105.775 6.001 212P 106.569 6.003 213P 106.569 6.001 213P 1	112P	105.237	6.035	4.005
121P105.440 6.033 122P105.970 6.031 1331P106.029 6.026 1331P104.967 6.026 1332P104.967 6.026 1332P104.967 6.026 1332P104.967 6.024 1351P105.191 6.024 1551P105.530 6.024 1551P105.530 6.024 1551P105.530 6.006 1551P105.530 6.006 1552P105.5690 6.006 152P105.5690 6.003 161P105.690 6.003 162P105.5690 6.003 151P105.578 6.003 161P105.690 6.001 211P105.778 6.002 211P105.578 6.003 312P105.578 6.003 312P105.578 6.003 312P105.578 6.003 312P105.578 6.003 312P105.578 6.001 312P105.578 6.003 312P106.578 6.001 312P105.379 5.998 312P105.379 5.998 312P105.379 5.998 312P107.257 5.998 312P107.257 5.998 312P107.257 5.998	113P	105.189	6.029	4.004
1122P 105.368 6.025 1131P 106.029 6.031 1131P 106.029 6.031 1131P 106.029 6.031 1131P 106.029 6.031 1131P 104.967 6.014 1141P 105.145 6.024 1152P 103.752 6.024 1152P 105.530 6.024 1152P 105.578 6.006 1152P 105.578 6.006 1153P 105.578 6.006 1163P 105.5690 6.006 1163P 105.578 6.002 1163P 105.5690 6.003 1163P 105.578 6.001 1163P 105.5690 6.000 117P 105.578 6.010 104.917 6.001 6.001 117P 105.578 6.001 104.917 6.001 6.001 105.578 6.001 6.001 105.579 6.001 6.001 105.379 5.988 6.011 <t< td=""><td>121P</td><td>105.440</td><td>6.033</td><td>4.008</td></t<>	121P	105.440	6.033	4.008
112.3P 1105.970 6.031 113.3P 106.029 6.026 114.1P 106.029 6.029 114.1P 105.145 6.029 114.1P 105.145 6.024 114.2P 105.145 6.024 114.1P 105.145 6.024 114.1P 105.191 6.025 115.2P 105.530 6.026 115.3P 105.573 6.026 116.3P 105.5690 6.006 116.3P 105.690 6.003 116.3P 105.690 6.000 116.3P 105.690 6.000 116.1P 105.690 6.010 213P 104.917 6.010 213P 106.127 6.010 213P 106.528 6.010 213P 106.377 6.010 213P 105.920 6.001 213P 105.046 6.001 213P 105.920 6.010 213P 105.920 5.982 213P 105.379 5.982	3122P	105.368	6.025	4.010
131P 106.029 6.026 132P 104.967 6.024 141P 105.191 6.023 142P 103.145 6.024 1141P 105.191 6.024 1142P 103.752 6.024 1143P 103.752 6.024 1143P 103.752 6.006 1153P 106.530 6.006 1163P 105.690 6.006 1163P 105.690 6.003 1163P 105.690 6.003 1163P 105.690 6.002 1163P 105.044 6.010 213P 104.917 6.010 213P 106.127 6.010 213P 106.127 6.010 213P 106.538 6.010 213P 106.127 6.001 213P 106.379 5.998 213P 105.920 6.011 213P 105.920 5.998 213P 105.379 5.998 213P 105.379 5.998 213P 105.379 5.998 213P 107.257 5.998 214 5.005 5.998	3123P	105.970	6.031	4.004
1132P 104.775 6.022 1141P 105.145 6.014 1142P 105.145 6.014 1142P 105.145 6.014 1142P 105.191 6.023 1142P 105.191 6.024 1152P 106.530 6.006 1152P 106.530 6.006 1162P 105.604 6.003 1163P 105.076 6.003 1163P 105.076 6.000 1163P 105.044 6.002 1163P 105.044 6.010 2113P 106.538 6.010 2113P 106.127 6.001 2113P 106.538 6.010 2113P 106.538 6.010 2133P 106.127 6.001 2133P 106.330 5.998 2133P 105.046 6.001 2133P 105.379 5.998 2133P 107.257 5.098 2133P 107.257	3131P	106.029	6.026	4.010
1133P 104.967 6.014 1141P 105.145 6.024 1143P 105.145 6.024 1152P 105.191 6.024 1153P 105.530 6.006 1153P 106.778 6.006 1163P 105.604 6.003 1163P 105.604 6.003 1163P 105.604 6.003 1163P 105.775 6.003 1163P 105.044 6.002 111P 105.044 6.003 111P 106.558 6.010 213P 104.744 6.001 213P 106.538 6.010 213P 106.538 5.998 213P 105.379 5.998 213P 105.379 5.998 213P 105.379 5.998 213P 107.257 5.998 213P 107.257 5.998	132P	104.775	6.022	4.005
141P 105.145 6.029 143P 105.191 6.024 1551P 106.730 6.024 1551P 106.778 6.006 1551P 106.778 6.006 1551P 105.670 6.006 1551P 105.778 6.003 1551P 105.670 6.006 1552P 105.678 6.003 1552P 105.670 6.003 1552P 105.775 6.003 211P 105.604 6.001 211P 104.917 6.010 211P 105.604 6.001 211P 106.558 6.010 211P 106.558 6.011 211P 106.560 6.011 211P 106.578 6.001 211P 106.558 6.011 211P 106.560 6.011 211P 106.579 6.001 211P 105.379 5.998 212P 105.379 5.998 212P 105.379 5.998 212P 107.257 5.098 212P 107.257 5.998	133P	104.967	6.014	4.011
142P 105.191 6.024 143P 105.530 6.006 152P 106.530 6.006 153P 105.573 5.955 161P 105.573 6.006 163P 105.690 6.006 163P 105.690 6.003 163P 105.690 6.003 163P 105.690 6.003 211P 105.690 6.003 212P 104.917 6.010 212P 104.917 6.010 212P 104.544 6.010 212P 106.558 6.011 212P 106.558 6.011 212P 106.560 6.001 212P 106.588 6.011 212P 106.588 6.011 212P 106.588 6.011 212P 106.588 6.011 212P 106.598 6.001 212P 106.598 5.998 213P 105.379 5.998 213P 107.257 5.982 217 107.257 5.982 217 5.998 5.998 217 5.905 5.998	:141P	105.145	6.029	4.006
143P 103.752 5.955 153P 106.530 6.006 153P 106.530 6.006 164P 105.970 6.006 165P 105.604 6.003 164P 105.604 6.003 165P 105.778 6.003 165P 105.604 6.003 165P 105.614 6.002 165P 105.775 6.010 213P 104.917 6.012 213P 104.917 6.012 213P 104.917 6.010 213P 106.538 6.010 213P 106.538 6.010 213P 106.538 6.010 213P 106.538 6.010 213P 105.546 6.001 213P 105.528 6.010 213P 106.5379 5.982 211P 105.920 6.011 212P 105.920 5.982 212P 107.257 5.982 27P 107.257 5.982	:142P	105.191	6.024	4.006
151P 106.530 6.006 153P 106.530 6.006 161P 105.604 6.003 162P 105.604 6.003 162P 105.604 6.003 162P 105.614 6.003 163P 105.775 6.003 164P 105.775 6.010 165P 105.775 6.010 213P 104.917 6.012 213P 104.744 6.010 213P 106.538 6.010 213P 106.544 6.001 213P 106.538 6.010 213P 106.5046 6.001 213P 106.5046 6.001 213P 105.920 6.010 213P 105.920 6.010 213P 105.920 6.010 213P 105.920 5.982 213P 107.257 5.982 27P 107.257 5.982	C143P	103.752	5.955	4.010
115.2P 106.778 6.006 116.3P 105.690 6.003 116.3P 105.690 6.003 116.3P 105.690 6.003 116.3P 105.690 6.002 2112P 105.041 6.010 2113P 104.744 6.010 3113P 104.744 6.010 3113P 106.127 6.001 3113P 106.160 6.001 3113P 106.160 6.001 3113P 105.960 6.010 3113P 105.920 6.011 3121P 105.920 6.011 3131P 105.960 6.011 3131P 105.920 6.010 3131P 105.920 6.010 3131P 105.920 5.998 3132P 107.257 5.998 3239 5.998 5.998	1151P	106.530	6.006	4.015
115.3P 105.970 6.003 116.1P 105.690 6.002 116.3P 105.690 6.002 116.3P 105.690 6.002 116.3P 105.690 6.002 213P 104.917 6.010 213P 104.917 6.010 213P 104.744 6.010 3412P 106.558 6.010 3412P 106.127 6.001 3412P 106.127 6.001 3412P 106.127 6.001 3412P 106.558 6.010 3412P 106.5127 6.001 3412P 105.060 6.011 3412P 105.920 6.011 3412P 105.920 6.011 3413P 105.379 5.998 373P 107.257 5.998 373P 107.257 5.093	152P	106.778	6.006	4.015
161P 105.604 6.002 1162P 105.690 6.008 1163P 105.775 6.002 213P 105.775 6.010 213P 105.775 6.010 213P 104.744 6.002 213P 104.744 6.010 213P 104.744 6.010 213P 106.558 6.010 213P 106.558 6.010 213P 106.127 6.001 213P 106.6558 6.010 213P 106.6160 6.011 213P 105.060 6.011 213P 105.370 5.998 27P 107.257 5.902 273P 107.257 6.005	153P	105.970	6.003	4.017
XI62P 105.690 6.008 2211P 105.775 6.002 2212P 105.775 6.001 2212P 105.775 6.002 311P 104.917 6.010 312P 104.917 6.011 313P 104.744 6.006 313P 106.558 6.010 313P 106.558 6.010 313P 106.6127 6.000 313P 106.127 6.001 313P 105.060 6.010 313P 105.320 6.001 313P 105.379 5.998 313P 105.379 5.998 313P 105.379 5.998 317 107.257 6.005	3161P	105.604	6.002	4.007
163P 105.775 6.002 2213P 104.917 6.010 2213P 104.917 6.012 2411P 106.558 6.010 3412P 106.558 6.001 3413P 106.127 6.001 3413P 106.127 6.001 3413P 106.166 6.001 3413P 106.560 6.001 3413P 106.160 6.001 3413P 105.060 6.010 3413P 105.379 5.998 3712P 105.379 5.998 372P 107.257 6.005	2162P	105.690	6.008	4.006
2311P 104.917 6.010 2312P 104.0417 6.010 2411P 105.041 6.012 3412P 106.558 6.010 3413P 106.558 6.001 3413P 106.127 6.001 3413P 106.127 6.001 3413P 106.046 6.001 3413P 105.060 6.001 3413P 105.050 6.010 3413P 105.050 6.010 3413P 105.379 5.998 373P 107.257 5.098 373P 107.257 5.005	163P	105.775	6.002	4.007
212P 105.041 6.012 213P 104.744 6.006 7411P 106.558 6.006 711P 106.558 6.001 711P 106.046 6.001 711P 105.060 6.001 711P 105.060 6.010 711P 105.060 6.011 711P 105.379 5.998 72P 104.301 5.982 73P 107.257 6.005	211P	104.917	6.010	4.006
21.3P 104.744 6.006 7411P 106.558 6.010 7413P 106.558 6.010 711P 106.046 6.001 711P 105.060 6.001 711P 105.060 6.010 711P 105.379 5.998 72P 104.301 5.982 73P 107.257 6.005	:212P	105.041	6.012	4.004
7411P 106.558 6.010 7412P 106.58 6.010 7413P 106.127 6.001 7413P 106.046 6.001 2X12P 106.061 6.001 2X12P 105.060 6.010 2X12P 105.920 6.010 2X12P 105.920 6.010 2X12P 105.379 5.998 71P 107.257 6.005	213P	104.744	6.006	4.003
3412P 106.127 6.009 3413P 106.046 6.001 3413P 105.060 6.001 3413P 105.060 6.001 3413P 105.920 6.010 3413P 105.920 6.016 3413P 105.920 6.016 3413P 105.920 6.016 371P 105.379 5.998 72P 104.301 5.982 73P 107.257 6.005	C411P	106.558	6.010	4.009
34.3P 106.046 6.001 X11P 105.060 6.001 X12P 105.160 6.010 X13P 105.320 6.016 713P 105.370 5.998 72P 104.301 5.982 73P 107.257 6.005	3412P	106.127	6.009	4.005
XI1P 105.060 6.001 X12P 106.160 6.010 X13P 105.920 6.016 X13P 105.379 5.998 71P 105.379 5.988 72P 104.301 5.982 73P 107.257 6.005	3413P	106.046	6.001	4.012
X12P 106.160 6.010 X13P 105.920 6.016 X1P 105.379 5.998 71P 105.379 5.988 72P 104.301 5.982 73P 107.257 6.005	XIIP	105.060	6.001	4.010
X13P 105.920 6.016 71P 105.379 5.998 6.016 72P 104.301 5.982 73P 73P 107.257 6.005	X12P	106.160	6.010	4.015
71P 105.379 5.998 72P 104.301 5.982 73P 107.257 6.005	X13P	105.920	6.016	4.012
2 72P 104.301 5.982 2 73P 107.257 6.005	71P	105.379	5.998	4.018
2 73P 107.257 6.005	272P	104.301	5.982	4.001
	C 73P	107.257	6.005	4.035

TABLE D6-	-CI10 copper pane	ls exposed at L	os Angeles.
Panel ID	Initial Mass, g	Length, in.	Width, in.
12F111P	106.492	6.015	4.026
12F112P	105.719	6.006	4.024
12F113P	105.912	6.006	4.025
12F121P	106.003	5.991	4.026
I2F122P	105.927	6.012	4.025
12F123P	105.606	6.004	4.022
I2F131P	105.836	5.986	4.021
I2F132P	105.255	6.007	4.021
I2F133P	105.144	6.006	4.020
12F141P	105.579	6.001	4.025
I2F142P	104.805	5.978	4.003
I2F143P	104.514	5.969	4.005
12F151P	104.785	6.025	4.005
12F152P	105.430	6.001	4.014
12F153P	105.146	6.002	4.001
12F161P	104.968	6.003	4.011
I2F162P	104.726	5.995	4.005
I2F163P	106.200	6.004	4.013
12F211P	105.796	6.005	4.012
I2F212P	105.810	6009	3.998
12F213P	105.858	6009	4.004
I2F411P	106.476	6009	4.028
I2F412P	105.620	6.007	4.019
I2F413P	105.229	6.001	4.004
12FX11P	106.112	6.037	4.029
12FX12P	105.591	6.018	4.003
12FX13P	104.815	6.002	4.002
12F 71P	104.707	5.988	4.005
12F 72P	105.753	6.004	4.025
12F 73P	107.010	6.014	4.035

ed at	Width, in.	4.003	4.006	4.006	4.005	4.001	4.005	4.003	4.002	4.003	4.008	4.003	4.005	4.006	4.005	4.006	4.005	4,004	4.007	4.002	4.005	4.005	4.015	4.026	4.005	4.022	4,004	4.002	4.035	4.003	4.015
r panels expos Il Zone.	Length, in.	6.013	6.011	6.002	6.010	6.005	6.008	5.998	6.002	6.003	6.010	600.9	6.011	6.012	5.967	6.011	6.015	6.018	6.015	5.993	6.009	6.009	6.010	6.005	6.008	6.015	5.990	6.015	6.009	6.022	6.003
.E D5—C110 coppe Panama Cano	Initial Mass, g	104.954	105.388	104.994	105.343	105.611	105.975	105.119	104.693	105.097	105.100	105.420	105.827	106.055	104.359	105.454	105.321	105.242	105.306	104.670	104.896	104.875	106.196	105.532	105.271	105.270	104.825	105.931	105.167	104.628	105.040
TABL	Panel ID	I2E111P	12E112P	I2E113P	12E121P	I2E122P	12E123P	I2E131P	12E132P	12E133P	I2E141P	12E142P	I2E143P	12E151P	12E152P	I2E153P	12E161P	12E162P	12E163P	12E211P	12E212P	12E213P	I2E411P	12E412P	I2E413P	12EX11P	12EX12P	12EX13P	12E 71P	12E 72P	12E 73P

TABLE E1-Alum at Kure Bt	inum panels exposed each, 250 m.	TABLE E2—Alum at Newar	iinum panels exposed ik Kearney.
Panel ID	Initial Mass, g	Panel ID	Initial Mass, g
111A111P	68.9462	111811119	69.5945
I1A112P	69.5144	11B112P	69.0103
11A113P	69.1502	11B113P	68.3239
11A121P	69.0929	11B121P	68.8103
I1A122P	69.6107	11B122P	67.7786
I1A123P	69.0658	11B123P	67.7434
11A131P	69.9579	IIB131P	67.1217
[1A132P	68.7874	IIB132P	67.5857
11A133P	68.8688	I1B133P	67.4356
IIA14IP	69.1827	I1B141P	67.8018
11A142P	69.2924	I1B142P	68.0154
I1A143P	69.0825	I1B143P	67.1931
IIAISIP	69.3078	IIBI51P	68.1514
11A152P	68.9278	11B152P	69.1421
IIAIS3P	68,9789	11B153P	68.3356
IIA161P	69.2882	I1B161P	69.2554
11A162P	70.0396	I1B162P	69.6452
11A163P	69.7923	I1B163P	69.6675
11A211P	68.7790	IIB211P	69.2182
11A212P	69.4508	I1B212P	68.0817
11A213P	68.5869	I1B213P	68.4229
11A411P	69.4792	I1B411P	68.5773
11A412P	68.1185	I1B412P	68.1994
11A413P	68.6198	I1B413P	67.8067
IIAXIIP	68.7413	IIBXIIP	68.3999
IIAX12P	68.7541	11BX12P	68.5002
II AX 13P	69.7758	IIBX13P	68.2265
	69.9270	11B 71P	69.9470
11A 72P	70.5598	11B 72P	68.7616
11A 73P	68.4741	11B 73P	68.3054

Tables E1 through E6 contain data for each site where aluminum panels were exposed.

APPENDIX E

TABLE E3-Alum	inum panels exposed it Reyes.	TABLE E4–Alum at Research	inum panels exposed Triangle Park.
Panel ID	Initial Mass, g	Panel ID	Initial Mass, g
IICIIIP	69.6004	IIDIIIP	69.8857
11C112P	70.4693	IID112P	68.9322
11C113P	70.3117	11D113P	69.4813
11C121P	70.0436	IID121P	69.2784
11C122P	70.3192	11D122P	69.9946
11C123P	69.6981	11D123P	70.2226
11C131P	69.4697	IID131P	69.8667
11C132P	70.3338	11D132P	69.7210
11C133P	69.0753	IID133P	70.6760
IIC141P	68.8866	IID141P	69.9860
11C142P	68.0932	IID142P	70.5060
11C143P	69.2631	IID143P	70.6268
IICISIP	69.0136	IID151P	69.1995
11C152P	68.5314	IID152P	69.9507
11C153P	69.6651	IIDIS3P	69.2246
11C161P	70.0600	IID161P	68.4206
11C162P	69.4102	11D162P	69.3489
11C163P	68.6220	IID163P	69.3598
11C211P	67.9865	11D211P	69.1246
11C212P	69.3146	11D212P	68.5070
11C213P	69.7699	I1D213P	69.3008
IIC411P	69.3673	IID411P	69.7781
11C412P	69.5336	IID412P	68.8535
11C413P	69.6459	IID413P	68.6751
IICXIIP	69.6895	IIDXIIP	69.2899
I1CX12P	70.4379	IIDX12P	69.5537
IICX13P	70.4560	IIDX13P	69.4334
11C 71P	69.9552	IID 7IP	68.7249
11C 72P	68.4349	IID 72P	69.4012
IIC 73P	70.1682	11D 73P	69.7986

anels s.	fxə	
نو به	panels	les.
E E6—Aluminum at Los Angel	E E6-Aluminum	at Los Angei

TABLE	F1-Steel panels ex	cposed at Kure	Beach.	TABLE F	2—Steel panels expo	osed at Newark	Kearney.
Panel ID	Initial Mass, g	Length, in.	Width, in.	Panel ID	Initial Mass, g	Length, in.	Width, in.
I4A111P	121.64	6.002	3.945	14B111P	122.27	6.003	3.944
I4A112P	122.13	6.004	3.942	I4B112P	120.18	6.005	3.942
I4A113P	122.23	6.007	3.939	14B113P	122.09	6.003	3.939
14A121P	122.54	6.003	3.942	14B121P	123.09	5.998	3.939
14A122P	121.60	6.004	3.941	I4B122P	121.52	6.004	3.940
I4A123P	122.73	6.006	3.940	14B123P	123.29	6.004	3.945
14A131P	121.75	6.004	3.944	14B131P	120.21	6.004	3.941
I4A132P	121.77	6.002	3.942	I4B132P	121.14	6.003	3.941
14A133P	121.68	6.007	3.944	I4B133P	124.13	6.004	3.944
I4A141P	121.33	6.005	3.942	14B141P	123.94	6.002	3.941
14A 142P	122.39	6.001	3.939	14B142P	124.09	6.004	3.940
14A143P	121.28	6.002	3.942	14B143P	121.58	6.003	3.942
14A151P	123.41	6.004	3.938	14B151P	122.23	6.001	3.937
I4A152P	122.42	6.008	3.941	14B152P	121.67	6.002	3.940
I4A153P	122.93	6.008	3.943	14B153P	122.25	6.005	3.943
14A161P	122.49	6.005	3.948	14B161P	121.88	6.002	3.942
I4A162P	122.93	6.007	3.943	14B162P	121.81	6.003	3.943
I4A163P	122.73	5.993	3.942	I4B163P	123.39	6.005	3.939
I4A211P	121.96	6.005	3.940	14B211P	121.30	6.004	3.939
14A212P	121.82	6.005	3.943	14B212P	122.53	6.002	3.943
I4A213P	121.89	6.002	3.942	14B213P	120.96	6.005	3.939
I4A411P	122.60	6.004	3.941	I4B411P	120.63	5.999	3.942
I4A412P	122.22	6.005	3.941	I4B412P	119.88	6.001	3.942
I4A413P	123.06	6.005	3.944	14B413P	120.88	6.002	3.943
14AX11P	121.72	6.005	3.942	14BX11P	123.47	6.003	3.941
14AX12P	121.08	6.004	3.941	14BX12P	122.99	6.004	3.942
I4AX13P	121.99	6.005	3.940	14BX13P	122.04	6.003	3.940

Tables F1 through F6 contain data for each site where steel panels were exposed.

APPENDIX F

Point Reyes.
at
exposed
panels
3-Steel
LL TT
TABLE

Panel ID	Initial Mass, g	Length, in.	Width, in.
I4C111P	122.38	6.001	3.941
I4C112P	123.53	6.003	3.941
I4C113P	122.99	6.002	3.941
I4C121P	120.75	6.005	3.947
I4C122P	121.21	6.003	3.942
I4C123P	121.42	6.003	3.943
14C131P	121.41	6.004	3.949
14C132P	121.66	6.003	3.945
I4C133P	122.48	6.002	3.941
14C141P	121.34	6.005	3.948
I4C142P	121.58	6.005	3.941
I4C143P	122.19	6.002	3.941
14C151P	121.62	000.9	3.942
14C152P	121.97	6.005	3.947
14C153P	122.09	6.003	3.938
14C161P	122.36	6.006	3.946
14C162P	121.97	6.003	3.940
I4C163P	121.11	6.001	3.942
14C211P	123.34	5.996	3.943
I4C212P	122.88	6.003	3.942
I4C213P	121.82	6.005	3.944
[4C4] [P	121.82	6.003	3.943
I4C412P	121.08	000'9	3.942
I4C413P	122.56	6,005	3.946
I4CX11P	122.18	6.012	3.945
I4CX12P	122.16	6.003	3.949
14CX13P	120.94	6.007	3.944

TABLE F4	Steel panels exposed	l at Research T	riangle Park.
Panel ID	Initial Mass, g	Length, in.	Width, in.
[4D111P	121.89	6.006	3.945
I4D112P	121.79	6.004	3.942
14D113P	122.58	6.007	3.939
I4D121P	122.30	6.000	3.942
I4D122P	122.27	6.005	3.941
I4D123P	122.34	6.005	3.940
14D131P	121.54	6.006	3.944
I4D132P	123.04	6.005	3.942
I4D133P	122.03	6.003	3.944
I4D141P	121.55	6.009	3.942
I4D142P	121.95	6.004	3.939
I4D143P	123.03	6.003	3.942
14D151P	123.54	6.003	3.938
I4D152P	122.41	6.005	3.941
I4D153P	122.46	6.006	3.943
I4D161P	122.09	6.004	3.948
14D162P	121.50	6.001	3.943
I4D163P	121.79	5.997	3.942
I4D211P	121.89	6.018	3.940
I4D212P	123.50	6.000	3.943
I4D213P	122.31	5.994	3.942
I4D411P	121.48	6.005	3.941
I4D412P	121.50	6.006	3.941
I4D413P	121.40	6.003	3.944
I4DX11P	121.12	6.005	3.942
14DX12P	123.13	6.002	3.941
I4DX13P	123.15	6.005	3.940

Ir Ste	el panels expos ittial Mass, g	ed at Panama (Length, in.	<i>Canal Zone.</i> Width, in.	TABLE Panel ID	F6Steel panels ex Initial Mass, g	<i>xposed at Los A</i> Length, in.	<i>Width, in.</i>
121.67		6 00.9	3.948	14F111P	171.70	6 007	3 940
122.70		6.001	3.942	14F112P	121.76	6.003	3.943
122.78		6.002	3.941	I4F113P	122.04	6.005	3.941
121.77		6.003	3.942	I4F121P	122.80	6.001	3.940
123.35		6.005	3.941	14F122P	123.30	6.005	3.941
122.60		5.995	3.939	I4F123P	121.18	6.003	3.940
122.07		6.003	3.941	I4F131P	121.18	6.007	3.940
122.07		6.005	3.940	I4F132P	122.58	6.051	3.940
122.83		6.007	3.945	I4F133P	124.01	6.049	3.943
121.59		6.005	3.940	[4F141P	123.71	6.049	3.944
121.22		6.008	3.940	I4F142P	120.93	6.027	3.942
121.25		6.005	3.939	I4F143P	123.13	6,038	3.940
120.40		6.005	3.942	I4F151P	121.48	5.984	3.941
121.31		6.002	3.940	I4F152P	120.41	5.973	3.938
121.41		6.002	3.943	I4F153P	122.11	6.050	3.938
121.50		6.006	3.940	I4F161P	122.37	6.046	3.941
122.12		6.000	3.944	I4F162P	122.73	6.051	3.941
121.42		6.005	3.941	14F163P	122.86	6.029	3.941
122.17		6.005	3.942	14F211P	122.72	6.053	3.942
122.23		6.008	3.942	14F212P	122.60	6.004	3.944
122.53		6.004	3.941	I4F213P	122.27	6.028	3.941
122.88		6.004	3.943	[4F411P	121.46	6.005	3.941
122.84		6.005	3.942	I4F412P	121.12	6.005	3.944
120.56		6.004	3.940	I4F413P	121.61	6.003	3.942
122.58		5.999	3.942	14FX11P	120.94	6.001	3.940
122.98		6.002	3.940	I4FX12P	122.16	6.005	3.940
121.69		6.003	3.939	[4FX13P	122.23	6.003	3.943

DEAN ON THE ATMOSPHERIC EXPOSURE PROGRAM 407

			Location"		Newark Kearney	diameter 0.115 in.)
Helix ID	Initial Mass, g	Rack	Column	Row	Helix ID	Initial Mass, g
13A111H	47.678	NB 51	-	V	1201111	
13A112H	47.974	NB 51	œ	A		40.10320
13A113H	48.202	NB 51	0	•		50.4/403
HICIAE	48 247				136113H	48.34322
13A177H	48 006				13B121H	47.89310
[3A123H	48 040				13B122H	50.17870
134131H	48 031				138123H	48.03188
	100.04				I3B131H	47.99065
	47.001				I3B132H	47.95109
	40.145				I3B133H	47.87934
13A141H	48.050				I3B141H	47.97358
13A142H	48.1/1				I3B142H	48,19695
13A143H	47.726				13B143H	47.77877
HISIAL	49.8/1				13B151H	48.02838
IJAI52H	47.812				I3B152H	47.77037
HSCIACI	101.05				13B153H	48.29124
13A 161H	48.348				[3R161H	47 66757
13A162H	48.194				13B162H	47 88467
13A163H	47.875				13B163H	47 97100
(3A211H	47.856	NB S1	7	J	IJRJIH	47 00011
[3A212H	48.054	NB 51	æ	c	ISBUTH	17667.14 80020 LV
(3A213H	47.058	NB 51	6	C	1387131	07/00.11
13A411H	45.867	NB 51	7	D		200/0°/L
(3A412H	48.014	NB 51	œ		H1158C1	4/.4458
13A413H	47.685	NR 51			13B412H	41.99108
13 A X 11 H	50.871		· r	ם נ	I3B413H	47.48402
ISAV17H	120.00		- 0	1	IJBX11H	47.41466
	00.00		0 0	L) [13BX12H	48.10135
HUIVACI	48,202	IC BN	ĥ	л	13RX13H	48 00038

Tables G1 through G5 contain data for each site where zinc helices were exposed.

APPENDIX G

Zinc helices exposed at	na Canal Zone.	Initial Mass, g	47.9343	48.0184	47.7174	48.2205	47.7320	47.3899	48.1694	48.3643	48.1009	48.0148	48.0551	47.9932	48.0081	48.0928	48.1490	48.0471	47.7788	48.0865	48.3548	48.1971	48.1442	47.9560	48.0951	47.8668	48.2107	47.9640	47.5104	
TABLE G5-	Pana	Helix ID	13E111H	I3E112H	I3E113H	I3E121H	I3E122H	I3E123H	I3E131H	I3E132H	I3E133H	I3E141H	I3E142H	I3E143H	I3E151H	13E152H	I3E153H	I3E161H	13E162H	I3E163H	I3E211H	I3E212H	I3E213H	I3E411H	I3E412H	I3E413H	13EX11H	I3EX12H	13EX13H	
nc helices exposed at	Triangle Park.	Initial Mass, g	47.7300	49.8518	48.1851	47.4688	47.2713	48.3204	48.0949	48.2304	48.1284	48.3627	47.6881	48.1338	50.2095	47.7630	48.2016	49.9425	48.0484	48.3418	50.2698	47.8681	47.8189	48.4075	47.5017	47.5146	47.8026	48.1058	47.7363	
TABLE G4—Zi	Research	Helix ID	I3D111H	I3D112H	13D113H	I3D121H	I3D122H	13D123H	I3D131H	I3D132H	13D133H	I3D141H	I3D142H	I3D143H	13D151H	13D152H	I3D153H	I3D161H	I3D162H	I3D163H	13D211H	I3D212H	13D213H	I3D411H	I3D412H	I3D413H	13DX11H	13DX12H	13DX13H	
helices exposed at Reyes.	Initial Mass, g	48.3453	48.1526	46.1/36	43.3460	41.9214	41.1911												48 0544	A551 84	FUCT-04	40.1004 47 8040	C3CC 84	0000 14	00006.14 8,009.74	47.0714 1157 7A	110/./2	49.093/		
TABLE G3-Zinc Point	Helix ID	13C111H	13C112H	13C113H			13012311	1101201	1201201			13C142H	1301510		11201201	1301511	1301001	11071001 H701001	130210	13/2171	1312751	13/1110		1303120			11/1/2/1	13CA13H	13C 72H	I3C 73H

TABLE	H1—Copper helices	exposed at K1	ire Beach, 25() m.		
			Location"		TABLE H2—Copp Newark Kearney (er helices exposed at (diameter 0.110 in.).
Helix ID	Initial Mass, g	Rack	Column	Row	Helix ID	Initial Mass, g
12A111H	68.171	NB 51		A		
12A112H	67.976	NB 51	7	A		68.0/4/1
I2A113H	68.174	NB SI	e	Α		0/.8/420
I2A121H	68.247					/76/97/0
I2A122H	67.982					6/./1/52
12A123H	68.107				H2C18C1	0/.81428 67 80045
12A131H	68.035					01000 23
12A132H	67.692				1121211	01.4321U
12A133H	67.622				1201221	1400/10
I2A141H	67.807					00660.00
12A142H	64.69				12B141H	68.16510
12A143H	68.199				12B142H	67.70503
12A151H	002 89				128143H	68.10885
17A157H	67.656				12B151H	68.17184
17A153H	507 TA				12B152H	68.20576
17A161H	67.060				I2B153H	68.05921
1101071	67.080				I2B161H	68.13775
170163H	68,000				I2B162H	68.14592
17A711H	68 074	NR 51	-	ر	I2B163H	68.18214
	67 160	15 an	-	יכ	12B211H	68.17135
12A213H	67.075	NR 51	، ۱		12B212H	68.09454
12A411H	67.565	NR 51	n -		12B213H	67.80559
HCIPVCI	68 175		• ~		12B411H	67.84990
	641.00		1 6	ב ב	I2B412H	67.70493
	67 046		، د	יי ב	I2B413H	67.68419
	044.10		- (មាដ	12BX11H	67.61710
	07/.00		7 0	ц	12BX12H	67.96542
IZAX13H	0/.5/3	NB SI	m	ш	12BX13H	67.70064
"NOTE: Only tions.	helices exposed on	13 January 1	987 have exp	osure loca-		

Tables H1 through H5 contain data for each site where copper helices were exposed.

APPENDIX H

-Copper helices exposed at	nama Canal Zone.	D Initial Mass, g	H 67.8257	H 68.0497	H 67.7585	H 68.0866	H 68.2306	H 67.6287	H 68.0287	H 68.2135	H 67.7324	H 67.6984	H 67.8424	H 67.0751	H 68.1114	H 67.7257	H 68.0457	H 68.2218	.H 68.1360	H 68.1540	H 67.9087	H 68.6505	H 68.5869	H 67.5993	H 67.5855	H 68.0618	1H 67.7495	2H 68.2866	3H 68.0341
TABLE H5-	Par	Helix II	I2E111	I2E112	I2E1131	[2E121]	I2E122	I2E123	I2E131	I2E1321	12E133	I2E141	I2E142	I2E143	I2E1511	I2E152	[2E153]	I2E161	I2E162	I2E163	I2E211	12E212	I2E213	I2E411	I2E412	I2E413	12EX11	12EX12	12EX13
pper helices exposed at	Triangle Park.	Initial Mass, g	68.0306	67 8137	68.0267	68.0240	67.8691	68.3496	67.8303	68.0443	67.5548	67.5809	67.9506	67.7961	67.8825	68.0743	68.0392	62.9899	68.0679	67.6124	68.0913	68.0798	67.7841	67.9776	68.1946	67.4977	67.8156	68.3595	68.1516
TABLE H4Cor	Research	Helix ID	HIIIQCI	HCIIUCI	12D113H	I2D121H	12D122H	12D123H	I2D131H	12D132H	12D133H	I2D141H	I2D142H	12D143H	12D151H	12D152H	12D153H	I2D161H	12D162H	I2D163H	I2D211H	12D212H	I2D213H	12D411H	I2D412H	12D413H	12DX11H	I2DX12H	I2DX13H
r helices exposed at Reyes.	Initial Mass, g	67.7346	68.4637	68.6932	67.8672	6/.8/51	67.9489													08.0455	0/.8042	00.0001	066870	0/.8242	68.0658 7 0700	67.9589	67.9701	67.5909	
TABLE H3—Copper Point l	Helix ID	12C111H	I2C112H	12C113H	IZCIZIH	12C122H	12C123H	1201311	12013211	1201331	12C141H	12C142H	120143H	HIGIDZI	IZCI 2ZH	HSCI23H		H201721			17/212H	120213H	12C411H	12C512H	12C413H	IZCXIIH	IZCX12H	12CX13H	12C 72H

DEAN ON THE ATMOSPHERIC EXPOSURE PROGRAM 411

TABLE	1-Aluminum helice	s exposed at h	Kure Beach, 2:	50 m.		:
			Location ^a		I ABLE 12–Alumii Newark Kearney (num netices exposed at diameter, 0.113 in.).
Helix ID	Initial Mass, g	Rack	Column	Row	Hefix ID	Initial Mass, g
IIAIIIH	17.8909	NB 51	10	A	IIBIIIH	19.62090
IIA112H	17.8749	NB 51	11	А	IIB112H	19.47712
IIA113H	17.9312	NB 51	12	A	IIB113H	20.53463
I1A121H	17.9783				IIB121H	18.00698
I1A122H	17.8341				I1B122H	19.67122
IIA123H	17.9061				I1B123H	17.86092
IIA131H	17.8934				IIB131H	19.68599
I1A132H	17.9425				I1B132H	19.59111
I1A133H	17.9989				I1B133H	19.58584
I1A141H	17.8734				IIB141H	21.10754
I1A142H	17.9377				I1B142H	19.82138
IIA143H	17.8800				I1B143H	19.53106
I1A151H	18.0190				IIBISIH	17.96578
IIAI52H	17.9845				I1B1S2H	19.63118
IIA153H	17.9147				IIBIS3H	21.38209
IIA161H	17.9977				IIB161H	19.69725
I1A162H	18.0091				I1B162H	21.13381
IIA163H	17.9766				IIB163H	20.90952
IIA2IIH	17.8898	NB 51	10	U	I1B211H	21.42692
11A212H	17.8867	NB 51	11	C	I1B212H	19.69654
IIA213H	17.9205	NB 51	12	C	I1B213H	19.59153
IIA411H	17.8202	NB 51	10	Ω	IIB411H	20.57725
IIA412H	17.9381	NB 51	11	Ω	I1B412H	19.53617
I1A413H	17.9166	NB 51	12	Ω	I1B413H	19.53516
IIAXIIH	17.8475	NB 51	10	ш	IIBXIIH	19.72094
IIAX12H	17.9037	NB 51	11	ы	II BX 12H	21.32137
II AX13H	17.8872	NB 51	12	Э	IIBX13H	19.74578
"Note: Onl	y helices exposed on	13 Jan. 1986 h	lave exposure	locations.		

Tables I1 through I5 contain data for each site where aluminum helices were exposed.

APPENDIX I

inum helices exposed at	Canal Zone.	Initial Mass, g	17.8254	18.1089	17.8704	17.9631	17.9311	17.9327	17.8186	18.0510	17.8936	17.1943	17.8093	17.8574	17.7824	17.9189	17.8319	17.9445	17.8085	17.9513	17.9620	17.8447	17.9869	17.8686	17.9079	17.7621	17.9828	17.7856	17.9728	
TABLE IS—Alum	Panama	Helix ID	IIEIIIH	11E112H	IIE113H	IIE121H	11E122H	11E123H	11E131H	I1E132H	11E133H	11E141H	11E142H	I1E143H	11E151H	11E152H	11E153H	11E161H	11E162H	11E163H	I1E211H	11E212H	11E213H	11E411H	11E412H	I1E413H	IIEXIIH	IIEX12H	11EX13H	
um helices exposed at	iangle Park.	Initial Mass, g	17.9200	17.9829	17.8066	17.9246	17.8919	17.8744	17.8425	17.9016	17.8449	17.8334	17.7424	17.8383	17.9203	17.9436	17.8233	17.8470	18.0348	17.8626	17.8982	17.9277	17.8705	17.9023	17.9504	17.9346	17,9160	18.0143	17.9912	
TABLE 14—Alumin	Research Tr	Helix ID	HIIIUII	11D112H	11D113H	IID121H	11D122H	11D123H	IID131H	I1D132H	I1D133H	IID141H	11D142H	11D143H	IID151H	11D152H	11D153H	11D161H	11D162H	I1D163H	11D211H	11D212H	11D213H	11D411H	11D412H	11D413H	IIDXIIH	11DX12H	11DX13H	
Reyes.	Initial Mass, g	21.3505	20.3517	19.5542	C6C0.61	19.0123	21.3329												11 5506	0400-17	150/.61	7007.17	19./000	0000.41	2100.12 1011 10	21.4164	C106.12	1 .344 /		
Point	Helix ID	IICIIIH	IIC112H	ILCIUM		11/12/1	11/1230	HCI2IB 11C120B	11/11/201				11/143/1								11/2/17	11/11/11			11/2/13/1				11C 72H	IIC /3H

TABLE 13-- Aluminum helices exposed at Doint Revos

Helix IDInitial Mass.Location*Location*Location*Helix IDInitial Mass.RackColumnRowHelix IDInitial Mass.14A112H24.307NB 515A14B112H24.4323914A112H24.3156A14B112H24.300314A112H24.325NB 515A14B112H24.300314A12H24.325NB 515A14B112H24.300314A12H24.325NB 516A14B12H24.300314A13H24.325NB 516A14B12H24.300314A13H24.23314B12H24.303614B13H24.1000314A13H24.23614B13H24.200314B13H24.270314A13H24.23614B13H24.270314B13H24.270314A13H24.23614B13H24.270314B13H24.270314A13H24.33614B13H24.270314B13H24.270314A13H24.33614B13H24.270314B13H24.270314A13H24.33614B13H24.329314213H24.270314A13H24.34614B13H24.371424.270314A13H24.34614B13H24.371424.270314A13H24.34614B13H24.371424.373314A13H24.34814B13H24.376414B13H24.379314A13H24.34614B13H24.347914812H24.349314A13H <td< th=""><th>TABL</th><th>E J1–Steel helices e</th><th>cposed at Kur</th><th>e Beach, 250 i</th><th>и.</th><th>TARIE 17- Ct.</th><th>the burner of the burner of the</th></td<>	TABL	E J1–Steel helices e	cposed at Kur	e Beach, 250 i	и.	TARIE 17- Ct.	the burner of the burner of the
Helix ID Initial Mass, g Rack Column Row Helix ID Initial Mass, g 14A11H 24.301 NB 51 5 A 14B111H 24.4323 14A112H 24.302 NB 51 5 A 14B112H 24.4323 14A112H 24.307 NB 51 5 A 14B112H 24.4323 14A12H 24.307 NB 51 5 A 14B12H 24.4323 14A12H 24.307 14B12H 24.3076 14B12H 24.3093 14A12H 24.307 14B12H 24.2046 14B12H 24.2093 14A12H 24.2133 14B12H 24.2093 14B132H 24.2093 14A12H 24.2133 14B12H 24.2093 14B132H 24.2093 14A12H 24.233 14B132H 24.2093 14B132H 24.2093 14A12H 24.243 14B12H 24.2454 24.2093 14B132H 24.2093 14A12H 24.243 14A12H 24.2454				Location ^a		Newark Kearney (a neuces exposed at diameter, 0.075 in.).
IA111H 24.381 NB 51 4 A I4B111H 24.4329 IAA112H 24.307 NB 51 5 A I4B112H 24.4329 IAA112H 24.307 NB 51 5 A I4B112H 24.4329 IAA12H 24.332 NB 51 6 A I4B112H 24.4329 IAA12H 24.315 5 A I4B12H 24.3068 IAA12H 24.315 5 A I4B12H 24.3068 IAA13H 24.313 14B132H 24.3093 I4B132H 24.3093 IAA13H 24.513 14B132H 24.239 I4B132H 24.2393 IAA13H 24.513 14B132H 24.3063 I4B132H 24.2393 IAA13H 24.2364 14B132H 24.3169 I4B132H 24.2393 IAA13H 24.3264 14B132H 24.3169 I4B132H 24.2393 IAA13H 24.326 14A13H 24.3169 I4B153H 24.3193 <td< th=""><th>Helix ID</th><th>Initial Mass, g</th><th>Rack</th><th>Column</th><th>Row</th><th>Helix ID</th><th>Initial Mass, g</th></td<>	Helix ID	Initial Mass, g	Rack	Column	Row	Helix ID	Initial Mass, g
IAA112H 24.307 NB 51 5 A IAB112H 24.00581 IAA112H 24.323 NB 51 6 A IAB113H 24.3038 IAA121H 24.345 IAB121H 24.354 IAB121H 24.3154 IAA121H 24.345 IAB121H 24.3154 IAB121H 24.3154 IAA121H 24.313 IAB121H 24.3153 IAB121H 24.3154 IAA131H 24.513 IAB121H 24.3154 IAB131H 24.2390 IAA131H 24.513 IAB131H 24.233 IAB132H 24.2393 IAA131H 24.513 IAB132H 24.2396 IAB132H 24.2393 IAA131H 24.364 IAB132H 24.2333 IAB141H 24.2393 IAA121H 24.364 IAB132H 24.2493 IAB132H 24.24936 IAA12H 24.364 IAB132H 24.364 IAB132H 24.24936 IAA12H 24.364 IAB132H 24.364 IAB133H 24.3664	I4A111H	24.381	NB 51	4	A	I4B111H	24.43239
IAA113H 24.323 NB 51 6 A IAB111H 24.39865 IAA121H 24.345 148121H 24.348 148121H 24.39865 IAA121H 24.345 148123H 24.438 24.358 24.358 IAA121H 24.445 148123H 24.438 24.358 IAA121H 24.167 148121H 24.10903 IAA132H 24.233 148121H 24.10903 IAA132H 24.233 148132H 24.2393 IAA141H 24.513 148132H 24.2393 IAA141H 24.233 148131H 24.2339 IAA141H 24.234 148131H 24.2339 IAA141H 24.346 148131H 24.2304 IAA15H 24.346 148131H 24.2304 IAA15H 24.346 148153H 24.3264 IAA15H 24.346 148153H 24.3264 IAA15H 24.346 148161H 24.3264 IAA15H 24.348 148161H	I4A112H	24.307	NB SI	5	A	I4B112H	24.00581
IAA121H 24.345 IAB121H 24.3965 IAA122H 24.517 24.315 148123H 24.2458 IAA123H 24.415 148123H 24.1534 24.1354 IAA131H 24.353 148133H 24.23930 24.1354 IAA132H 24.513 148133H 24.20930 148133H 24.20930 IAA132H 24.513 148133H 24.20930 148133H 24.20930 IAA141H 24.513 148133H 24.2093 148131H 24.20930 IAA142H 24.305 148131H 24.2093 148131H 24.2093 IAA141H 24.313 148151H 24.2093 148151H 24.2093 IAA151H 24.345 148151H 24.2093 148153H 24.2093 IAA151H 24.343 148153H 24.3263 148153H 24.3263 IAA162H 24.336 148153H 24.3263 148153H 24.3263 IAA151H 24.343 148153H 24.3264 148163H 24.3266 IAA162H 24.343 148163H 24.32673 14816	I4A113H	24.323	NB S1	ę	A	I4B113H	24.31148
IAA122H 24.517 IAA122H 24.4154 24.13544 IAA123H 24.415 [4B123H 24.10903 IAA131H 24.233 [4B123H 24.10903 IAA132H 24.233 [4B133H 24.23930 IAA133H 24.233 [4B131H 24.23930 IAA133H 24.236 [4B131H 24.23930 IAA133H 24.236 [4B131H 24.23930 IAA133H 24.236 [4B131H 24.23930 IAA133H 24.236 [4B141H 24.23930 IAA153H 24.236 [4B153H 24.23930 IAA153H 24.364 [4B153H 24.23930 IAA153H 24.365 [4B153H 24.23930 IAA153H 24.346 [4B153H 24.23930 IAA153H 24.346 [4B153H 24.23930 IAA153H 24.346 [4B153H 24.23930 IAA15H 24.346 [4B153H 24.23670 IAA15H 24.346 [4B153H 24.32670 IAA15H 24.343 [4B153H 24.32670 <	I4A121H	24.345				I4B121H	24.29865
IA123H 24.415 148123H 24.42458 IA131H 24.233 148131H 24.10903 IA132H 24.167 148131H 24.10903 IA132H 24.167 148131H 24.10903 IA132H 24.233 148131H 24.2395 IA141H 24.513 148131H 24.2395 IAA141H 24.513 148141H 24.2393 IAA142H 24.513 148141H 24.2393 IAA142H 24.513 148151H 24.2733 IAA151H 24.364 148151H 24.2733 IAA151H 24.364 148151H 24.2733 IAA151H 24.364 148151H 24.2733 IAA151H 24.364 148151H 24.2703 IAA151H 24.366 148151H 24.2703 IAA151H 24.313 148152H 24.24936 IAA151H 24.343 148151H 24.22634 IAA151H 24.343 148152H 24.23733 IAA15H 24.343 148152H 24.23733 IAA15H 24.343	I4A122H	24.517				I4B122H	24.13544
IA13IH 24.233 IA13IH 24.10903 IA132H 24.230 IA132H 24.10903 IA132H 24.513 IA132H 24.23930 IA132H 24.513 IA142H 24.513 IA141H 24.513 IA142H 24.513 IA141H 24.513 IA142H 24.23930 IA143H 24.513 IA142H 24.2143 IA143H 24.513 IA143H 24.2143 IA151H 24.245 IA143H 24.2143 IA151H 24.366 IA151H 24.2143 IA151H 24.366 IA151H 24.2143 IA151H 24.366 IA152H 24.2143 IA153H 24.366 IA153H 24.2143 IA151H 24.366 IA153H 24.2143 IA162H 24.366 IA162H 24.2333 IA162H 24.366 IA162H 24.201 IA15H 24.366 IA162H 24.2363 IA162H 24.366 IA162H 24.24936 IA162H 24.3437 IA162H 24.	I4A123H	24.415				I4B123H	24.42458
[4A132H] 24.167 [4B132H] 24.2296 [4A133H] 24.230 [4B133H] 24.2293 [4A141H] 24.513 [4B141H] 24.23930 [4A141H] 24.513 [4B141H] 24.23930 [4A141H] 24.313 [4B141H] 24.2393 [4A143H] 24.305 [4B141H] 24.2393 [4A151H] 24.364 [4B151H] 24.2493 [4A151H] 24.366 [4B151H] 24.2493 [4A153H] 24.307 [4B161H] 24.2493 [4A153H] 24.307 [4B161H] 24.2303 [4A161H] 24.307 [4B162H] 24.2303 [4A161H] 24.348 NB 51 4 C [4A213H] 24.348 NB 51 4 C [4A213H] 24.336 NB 51 4 24.2303 [4A213H] 24.336 NB 51 5 C 148213H 24.3377 [4A213H] 24.336 NB 51 6 C 148213H 24.33670 [4A213H] 24.348 NB 51 5 <t< td=""><td>I4A131H</td><td>24.233</td><td></td><td></td><td></td><td>I4B131H</td><td>24.10903</td></t<>	I4A131H	24.233				I4B131H	24.10903
IA133H 2.4.230 IA131H 2.4.230 IA141H 2.4.513 IA141H 2.4.23930 IA141H 2.4.513 IA141H 2.4.2395 IA141H 2.4.513 IA141H 2.4.2395 IA141H 2.4.513 IA141H 2.4.2395 IA141H 2.4.295 IA141H 2.4.2395 IA151H 2.4.364 IA151H 2.4.24936 IA153H 2.4.364 IA151H 2.4.24936 IA151H 2.4.307 IA161H 2.4.307 IAA161H 2.4.307 IA161H 2.4.307 IAA161H 2.4.307 IA163H 2.4.303 IAA161H 2.4.307 IA163H 2.4.307 IAA161H 2.4.307 IA162H 2.4.301 IAA162H 2.4.316 IA162H 2.4.301 IAA162H 2.4.336 IA163H 2.4.301 IAA162H 2.4.336 IA163H 2.4.301 IAA162H 2.4.348 IA813H 2.4.301 IAA162H 2.4.348 IA8213H 2.4.3041 IAA213H 2.4.430 </td <td>I4A132H</td> <td>24.167</td> <td></td> <td></td> <td></td> <td>I4B132H</td> <td>24.22296</td>	I4A132H	24.167				I4B132H	24.22296
[4A14]H 24.513 [4B14]H 24.2148 [4A142]H 24.245 [4B142]H 24.27339 [4A142]H 24.364 [4B15]H 24.27339 [4A15]H 24.364 [4B15]H 24.27339 [4A15]H 24.364 [4B15]H 24.24936 [4A15]H 24.364 [4B15]H 24.24936 [4A15]H 24.305 [4B15]H 24.33239 [4A16]H 24.305 [4B15]H 24.33239 [4A16]H 24.307 [4B16]H 24.33239 [4A16]H 24.348 [4B16]H 24.33239 [4A16]H 24.348 [4B16]H 24.33670 [4A16]H 24.348 [4B16]H 24.33670 [4A16]H 24.348 [4B16]H 24.33670 [4A213]H 24.347 [4B13]H 24.33670 [4A213]H 24.349 [4B13]H 24.33670 [4A213]H 24.347 [4B13]H 24.33670 [4A213]H 24.347 [4B13]H 24.33670 [4A213]H 24.347 [4B13]H 24.33670 [4A41]H <td>I4A133H</td> <td>24.230</td> <td></td> <td></td> <td></td> <td>I4B133H</td> <td>24.23930</td>	I4A133H	24.230				I4B133H	24.23930
I4A142H 24.295 I4B142H 24.2739 I4A143H 24.364 14B151H 24.2731 I4A151H 24.364 14B151H 24.27019 I4A151H 24.364 14B151H 24.27036 I4A151H 24.364 14B151H 24.31423 I4A151H 24.305 14B151H 24.31423 I4A151H 24.305 14B153H 24.31423 I4A151H 24.305 14B161H 24.33239 I4A163H 24.348 18B151H 24.33239 I4A163H 24.348 14B161H 24.33239 I4A163H 24.348 14B161H 24.33339 I4A163H 24.348 14B161H 24.3273 I4A163H 24.348 14B161H 24.32670 I4A213H 24.347 14B12H 24.2377 I4A213H 24.347 14B12H 24.24771 I4A213H 24.347 14B12H 24.24771 I4A213H 24.347 14B12H 24.24771 I4A213H 24.347 14B12H 24.24771 I4A413H 24.	I4A141H	24.513				I4B141H	24.21448
[4A143H] 24.242 [4B143H] 24.21019 [4A151H] 24.364 [4B151H] 24.3103 [4A152H] 24.364 [4B153H] 24.31433 [4A153H] 24.305 [4B153H] 24.31433 [4A153H] 24.306 [4B153H] 24.31433 [4A163H] 24.305 [4B161H] 24.33329 [4A163H] 24.343 [4B163H] 24.33329 [4A163H] 24.343 [4B163H] 24.33329 [4A163H] 24.343 [4B163H] 24.32333 [4A163H] 24.343 [4B163H] 24.3370 [4A163H] 24.343 [4B163H] 24.3203 [4A213H] 24.346 NB 51 4 C [4A213H] 24.346 NB 51 4 C [4A11H] 24.347 NB 51 4 D [4A411H] 24.347 NB 51	I4A142H	24.295				I4B142H	24.27339
IAISIH 24.364 [4B15]H 24.3222 IAIS2H 24.345 [4B15]H 24.245 IAIS2H 24.305 [4B15]H 24.3329 IAIS1H 24.307 [4B16]H 24.3329 IAAIS1H 24.403 [4B16]H 24.3329 IAAIS1H 24.413 [4B16]H 24.3329 IAAI51H 24.449 NB 51 4 24.2879 IAA131H 24.348 NB 51 4 24.2870 IAA211H 24.348 NB 51 5 C [4B16]H 24.23670 IAA213H 24.349 NB 51 5 C [4B211]H 24.42001 IAA213H 24.346 NB 51 5 C [4B13]H 24.33670 IAA213H 24.337 NB 51 6 C [4B213]H 24.33670 IAA413H 24.337 NB 51 6 D [4B413]H 24.33670 IAA411H 24.337 NB 51 6 D [4B413]H 24.33670 IAA411H 24.337 NB 51 6 D [4B413]H </td <td>I4A143H</td> <td>24.242</td> <td></td> <td></td> <td></td> <td>I4B143H</td> <td>24.21019</td>	I4A143H	24.242				I4B143H	24.21019
IA152H 24.245 IAB152H 24.245 24.24936 IA153H 24.305 IAB153H 24.307 24.31423 IAA153H 24.307 IAB161H 24.3329 IAA153H 24.307 IAB161H 24.3329 IAA153H 24.413 IAB162H 24.3233 IAA153H 24.348 IAB161H 24.23733 IAA151H 24.348 IAB163H 24.23733 IAA212H 24.113 NB 51 4 C I4B163H 24.23670 IAA213H 24.489 NB 51 5 C I4B213H 24.30414 IAA213H 24.336 NB 51 6 C I4B213H 24.33670 IAA413H 24.337 NB 51 6 D I4B411H 24.33670 IAA413H 24.337 NB 51 6 D I4B413H 24.33670 IAA413H 24.337 NB 51 6 D I4B413H 24.33670 IAA413H 24.337 NB 51	14A151H	24.364				I4B151H	24.22624
IA153H 24.305 I48153H 24.31423 IA161H 24.307 I48161H 24.3123 IA161H 24.413 I48161H 24.3329 IA163H 24.413 I48161H 24.3329 IA163H 24.413 I48161H 24.2233 IA163H 24.413 I48163H 24.2301 IA211H 24.489 NB 51 4 C IA213H 24.413 NB 51 5 C I48211H 24.23670 IA213H 24.336 NB 51 5 C I48213H 24.23670 IA412H 24.336 NB 51 6 C I48213H 24.23670 IA412H 24.336 NB 51 6 D I48113H 24.33676 IA412H 24.337 NB 51 6 D I48113H 24.33676 IA412H 24.337 NB 51 6 D I48113H 24.33676 IAA13H 24.337 NB 51 6 D I48113H 24.33676 IAA11H 24.337 NB 51 6 D <td>I4A152H</td> <td>24.245</td> <td></td> <td></td> <td></td> <td>I4B152H</td> <td>24.24936</td>	I4A152H	24.245				I4B152H	24.24936
I4A16IH 24.307 I4B161H 24.3329 I4A162H 24.413 I4B162H 24.3329 I4A162H 24.413 I4B163H 24.3329 I4A163H 24.348 IB51 24.2233 I4A153H 24.348 IB51 24.201 I4A12H 24.489 NB 51 5 C I4A213H 24.113 NB 51 5 C I4A213H 24.316 NB 51 5 C I4A213H 24.336 NB 51 6 C I4A12H 24.337 NB 51 6 D I4A413H 24.337 NB 51 6 D I4A413H 24.337 NB 51 6 D I4A413H 24.337 NB 51 6 D I4A13H 24.337 NB 51 6 D I4A13H 24.347 NB 51 6 D I4A13H 24.347 NB 51 6 D I4A13H 24.347 NB 51 6 D I4AX11H 24.347 NB 51	I4A153H	24.305				I4B153H	24.31423
14A162H 24.413 14B162H 24.22233 14A163H 24.348 14B163H 24.228795 14A163H 24.348 14B163H 24.228795 14A163H 24.489 NB 51 4 24.2233 14A163H 24.489 NB 51 4 24.22670 14A213H 24.4113 NB 51 5 C 14B213H 24.30414 14A213H 24.336 NB 51 5 C 14B213H 24.3371 14A413H 24.337 NB 51 6 D 14B412H 24.3371 14A413H 24.337 NB 51 6 D 14B412H 24.3371 14A413H 24.337 NB 51 6 D 14B412H 24.33067 14AA13H 24.337 NB 51 6 D 14B413H 24.33064 14AA13H 24.347 NB 51 6 D 14B413H 24.32064 14AX12H 24.347 NB 51 6 E 14AX13H	I4A161H	24.307				I4B161H	24.38329
IAA163H 24.348 IA8163H 24.348 24.348 24.28795 IAA211H 24.489 NB 51 4 C I48211H 24.42001 IAA212H 24.4113 NB 51 5 C I48213H 24.30414 IAA213H 24.113 NB 51 5 C I48213H 24.30414 IAA213H 24.336 NB 51 6 C I48213H 24.3071 IAA213H 24.336 NB 51 6 C I48213H 24.33670 IAA313H 24.420 NB 51 6 D I48412H 24.33677 IAA313H 24.337 NB 51 6 D I48413H 24.33677 IAA313H 24.347 NB 51 6 D I48413H 24.33677 IAA313H 24.347 NB 51 6 D I48413H 24.3367 IAA313H 24.347 NB 51 6 E I48713H 24.32064 IAAX12H 24.335 NB 51 <td>I4A162H</td> <td>24.413</td> <td></td> <td></td> <td></td> <td>I4B162H</td> <td>24.22233</td>	I4A162H	24.413				I4B162H	24.22233
I4A211H 24.489 NB 51 4 C I4B211H 24.42001 I4A212H 24.113 NB 51 5 C I4B212H 24.42001 I4A213H 24.113 NB 51 5 C I4B213H 24.23670 I4A213H 24.336 NB 51 6 C I4B213H 24.23670 I4A411H 24.336 NB 51 6 C I4B411H 24.24371 I4A413H 24.429 NB 51 6 D I4B412H 24.3367 I4A413H 24.337 NB 51 6 D I4B413H 24.3367 I4A11H 24.337 NB 51 6 D I4B413H 24.3367 I4A11H 24.347 NB 51 6 D I4B413H 24.3266 I4AX11H 24.347 NB 51 6 E I4BX11H 24.3204 I4AX12H 24.347 NB 51 6 E I4BX13H 24.3106 I4AX12H 24.347 NB	I4A163H	24.348				I4B163H	24.28795
I4A212H 24.113 NB 51 5 C I4B212H 24.23670 I4A213H 24.276 NB 51 6 C I4B213H 24.30414 I4A213H 24.376 NB 51 6 C I4B213H 24.30414 I4A411H 24.336 NB 51 4 D I4B411H 24.39267 I4A413H 24.429 NB 51 5 D I4B412H 24.39267 I4A413H 24.337 NB 51 6 D I4B413H 24.33674 I4A413H 24.337 NB 51 6 D I4B413H 24.33674 I4A413H 24.335 NB 51 6 D I4B413H 24.32064 I4AX12H 24.347 NB 51 6 E I4BX11H 24.32064 I4AX12H 24.347 NB 51 6 E I4BX13H 24.31066 I4AX13H 24.347 NB 51 6 E I4BX13H 24.3106 I4AX13H 24.347	I4A211H	24.489	NB 51	4	C	I4B211H	24.42001
I4A213H 24.276 NB 51 6 C I4B213H 24.3014 I4A411H 24.336 NB 51 4 D I4B411H 24.347 I4A411H 24.336 NB 51 4 D I4B411H 24.3971 I4A412H 24.429 NB 51 5 D I4B412H 24.3377 I4A413H 24.337 NB 51 6 D I4B413H 24.3274 I4A413H 24.337 NB 51 6 D I4B413H 24.3204 I4A11H 24.194 NB 51 6 D I4BX11H 24.3204 I4AX11H 24.194 NB 51 5 E I4BX11H 24.3204 I4AX12H 24.347 NB 51 6 E I4BX12H 24.3183 I4AX13H 24.347 NB 51 6 E I4BX13H 24.31183	I4A212H	24.113	NB 51	ŝ	C	I4B212H	24.23670
I4A411H 24.336 NB 51 4 D I4B411H 24.24371 I4A412H 24.429 NB 51 5 D I4B412H 24.39567 I4A412H 24.429 NB 51 5 D I4B412H 24.3377 I4A413H 24.337 NB 51 6 D I4B413H 24.3267 I4A413H 24.337 NB 51 6 D I4B413H 24.3204 I4A11H 24.194 NB 51 6 D I4BX11H 24.3204 I4AX12H 24.335 NB 51 5 E I4BX11H 24.3066 I4AX13H 24.347 NB 51 6 E I4BX13H 24.3183	I4A213H	24.276	NB 51	9	C	I4B213H	24.30414
IA412H 24.429 NB 51 5 D I4B412H 24.39267 IA413H 24.337 NB 51 6 D I4B413H 24.3374 IA413H 24.337 NB 51 6 D I4B413H 24.3267 IAA11H 24.194 NB 51 6 D I4BX11H 24.32004 IAX11H 24.135 NB 51 5 E I4BX12H 24.3004 IAX12H 24.335 NB 51 5 E I4BX12H 24.31206 IAX13H 24.347 NB 51 6 E I4BX13H 24.3178	I4A411H	24.336	NB 51	4	D	I4B411H	24.24371
I4A413H 24.337 NB 51 6 D I4B413H 24.23874 I4AX11H 24.194 NB 51 4 E I4BX11H 24.32004 I4AX12H 24.135 NB 51 5 E I4BX12H 24.31206 I4AX12H 24.335 NB 51 5 E I4BX12H 24.3106 I4AX13H 24.347 NB 51 6 E I4BX13H 24.3183	I4A412H	24.429	NB 51	S	D	I4B412H	24.39267
I4AXIIH 24.194 NB 51 4 E I4BX11H 24.32004 I4AX12H 24.335 NB 51 5 E I4BX12H 24.3206 I4AX12H 24.335 NB 51 5 E I4BX12H 24.3106 I4AX13H 24.347 NB 51 6 E I4BX13H 24.31183	I4A413H	24.337	NB 51	9	D	I4B413H	24.23874
I4AX12H 24.335 NB 51 5 E I4BX12H 24.12606 I4AX13H 24.347 NB 51 6 E I4BX13H 24.31183	I4AX11H	24.194	NB 51	4	ш	I4BX11H	24.32004
I4AX13H 24.347 NB 51 6 E I4BX13H 24.31183	I4AX12H	24.335	NB 51	ŝ	ш	I4BX12H	24.12606
	I4AX13H	24.347	NB 51	9	Е	I4BX13H	24.31183

APPENDIX J

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helices exposed at	anal Zone.	Initial Mass, g	24,1437	24.2014	24.2036	24.2914	24.1730	24.2221	24.3779	24.3048	24.4857	24.3446	24.4171	24.2651	24.3226	24.2114	24.2022	24.3094	24.2985	24.4182	24.3717	24.2773	24.4074	24.3398	24.3403	24.3320	24.3196	24.3450	24.5176	
TABLE J5—Steel	Panama C	Helix ID	I4E111H	I4E112H	I4E113H	I4E121H	I4E122H	I4E123H	I4E131H	I4E132H	I4E133H	I4E141H	I4E142H	I4E143H	I4E151H	I4E152H	I4E153H	I4E161H	I4E162H	I4E163H	I4E211H	I4E212H	I4E213H	I4E411H	I4E412H	I4E413H	I4EX11H	I4EX12H	I4EX13H	
helices exposed at	iangle Park.	Initial Mass, g	24.4183	24.2206	24.3455	24.1734	24.1875	24.3112	24.2550	24.3193	24.0940	24.4778	24.4062	24.2836	24.2266	24.3215	24.2141	24.3828	24.3786	24.3688	24.2752	24.4623	24.3466	24.2952	24.2541	24.3130	24.1740	24.4353	24.2948	
TABLE J4—Steel	Research Tr	Helix ID	I4D111H	I4D112H	I4D113H	I4D121H	I4D122H	I4D123H	I4D131H	I4D132H	I4D133H	I4D141H	I4D142H	I4D143H	I4D151H	I4D152H	I4D153H	I4D161H	I4D162H	I4D163H	I4D211H	I4D212H	I4D213H	[4D4] 1H	I4D412H	I4D413H	I4DX11H	I4DX12H	14DX13H	
	1	1																												
helices exposed at Reyes.	Initial Mass, g	24.4510	24.1635	24.2539	24.3092	24.1534	24.3801												470C 4C	4/07/47	24.0092	24.3393	24.2.00	0110.42	4001.42	1/07.42	2112.42 2100 AC	0407.47		
TABLE J3—Steel Point	Helix ID	I4C111H	I4C112H	I4C113H	14C121H	14C122H	14C123H	1401041	14013211	1401030	1401411	14C142H	1401431	INCIDEN	14010211	1401000		1401050	14/0101	1402120	14/21211	14/2130		14001211			14/17120		I4C 72H	I4C 73H

APPENDIX K

ISO CORRAG Collaborative Testing Program*

Introduction and the Aim of the Collaborative Testing Program ISO CORRAG

The determination of the corrosivity of a test site or area to be developed provides the basic information which allows for the evaluation of the tests as well as the selection of suitable corrosion-preventing measures to be taken. Four ISO/DP have been developed and form the framework of the activity of WG4.

1. ISO/DP 9223—Corrosion of Metals and Alloys—Classification of Corrosivity Categories of Atmospheres. Corrosion des méstaux et alliages—Classification des catégories de corrosivitié des atmosphères.

2. ISO/DP 9224—Corrosion of Metals and Alloys—Guiding Values for the Corrosivity Categories of Atmospheres. Corrosion des méstaux et alliages—Valuers directirices relatives aux catégories de corrosivité des atmosphères.

3. ISO/DP 9225—Corrosion of Metals and Alloys—Aggressivity of Atmospheres—Methods of Measurement of Pollution Data. Corrosion des métaux et alliages—Agressivité des atmosphères—Méthodes de mesurage des données relatives à la pollution.

4. ISO/DP 9226—Corrosion of Metals and Alloys—Corrosivity of Atmospheres—Methods of Determination of Corrosion Rate of Standard Specimens for the Evaluation of Corrosivity. Corrosion des métaux et alliages—Corrosivité des atmosphères—Méthodes des détermination de la vitesse de corrosion d'éprouvettes pour l'évaluation de la corrosivité.

These documents summarize the present knowledge of the classification of the corrosivity and of the methods for the measurement of decisive factors of environment and of the modes of the corrosivity determination of the corrosion test results and of the data of the wetness and atmosphere pollution.

The aim of the collaborative testing program is to verify the procedures applied in ISO/DP 9223, 9224, 9225, and 9226 and, furthermore, to build the data base for the proposal of methodical processes and classification diagrams which will be utilized in the working out of the first version of the collaborative standards.

The aim of the program consists in the studies of methodological and theoretical aspects of the procedures to be included in the proposals of international standards. The results of the exposure will give comparison of different direct methods for corrosivity determination and the atmospheric aggressivity evaluation using environmental data. Exposure on different locations in many countries according to the accepted basic principles represents an economical and rational basis for obtaining knowledge in corrosivity determination.

The fact that the corrosivity for the significant area of the earth which covers up various microclimatic zones with various pollution levels will be derived in a uniform mode, is of a great theoretical and technical importance. A collaborative program with a uniform methodology and specified materials has not been accomplished within the concerned extent.

Countries that participated in the collaborative testing program ISO CORRAG were as follows:

Canada Czechoslovakia Finland France Germany F.R. Japan

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Norway Spain Sweden UK USA USSR

1. Description of Collaborative Testing Program ISO CORRAG

1.1 Tested Materials

- unalloyed carbon steel,
- zinc,
- aluminum, and
- copper.

1.2 Types of Specimens

- flat plate specimens and
- metallic wire-open helix specimens.

1.3 Exposure Sequences (Fig. 5)

- 6 one-year exposures,
- 1 two-year exposure,
- 1 four-year exposure, and



FIG. 5—Exposure sequences.

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- 1 long-term exposure (ideally ten years).
- Total: 9 exposure sequences

NOTE: Three sets of specimens of each metal should be exposed for a year starting both in spring and autumn.

1.4 Scheme of Exposure Sequences for Test Specimens

Number of specimens for one material and one atmospheric corrosion test site: $(6 + 1 + 1 + 1) \times 3 = 27$; 3 specimens for every removal.

1.5 Category of Location

open air exposure

1.6 Beginning of Program

• Fall 1986

1.7 Supplementary Program

See Document WG4 N105. This program is of an ongoing character and it is recommended only, and it depends on the capabilities of the participant and/or collaborating parties which of the recommended suggestions will be included in the tests. Each of the participants who decides to carry out even some complimentary tests should plan them individually while taking the principles contained in the ISO/TC 156 documents into consideration.

2. Test Specimens

2.1 Types of Specimens

2.1.1 Flat Plate Specimens—The specimens are rectangular plates with dimensions of preferably 100 by 150 mm, at least 50 by 100 mm with a thickness of approximately 1 mm.

2.1.2 Metallic Wire—Open Helix Specimens—Wires with a diameter d of 2 to 3 mm are cut to a length of approximately 1000 mm. They are then rolled into a helix using a rod with diameter of 24 mm as a former. Helix holders are plastic rods made from polyamide or other inert material, length 100 mm, diameter 10 mm. For open helix specimen assembly see Fig. 6.



FIG. 6-Open helix specimen assembly.

2.2 Materials

- unalloyed carbon steel (Table K1),
- zinc min. 98.5,
- aluminum min. 99.85 (aluminum 99.5 is allowed), and
- copper min. 99.5.

The program will be uniformly supplied with

• steel flat specimens produced in the United Kingdom,

• open helix specimens of steel produced in the United Kingdom and formed in the Federal Republic of Germany, and

• open helix specimens of copper, zinc, and aluminum produced in the Federal Republic of Germany or provided by the participants.

Composition of helices of copper, zinc, and aluminum produced in the Federal Republic of Germany. The other materials provided by the participants are in accordance with given specifications.

2.3 Specimen Preparation

2.3.1 Marking—Marking should be legible and durable over the whole period of exposure. Flat plate specimens may be marked by stamping the appropriate numbers with a numbering stamp. Notched specimens or drilled holes can be used. The area affected by marking should be minimized. Open helix specimens will be marked on plastic rods.

The establishment is recommended of a reliable map of specimen identity, exposure data, and location on the exposure frame.

2.3.2 Number—Three specimens to be exposed simultaneously during each exposure, the total number of specimens of each type and each material will be 27.

2.3.3 Surface Cleaning Before Exposure—The samples before their exposure are to be degreased by the submerging into organic solvents or in their vapors, for example, acetone, trichloroethylene, dried and weighed with the accuracy for

- steel, zinc, and copper of 0.001 g and
- aluminum of 0.0001 g.

Component	Percent
Carbon	0.056
Silicon	0.060
Sulfur	0.012
Phosphorus	0.013
Chromium	0.02
Molybdenum	0.01
Nickel	0.04
Copper	0.03
Niobium	0.01
Titanium	0.01
Vanadium	0.01
Aluminum	0.02
Tin	0.005
Nitrogen	0.004
Manganese (X-ray fluorescence)	0.39

TABLE K1—Composition & unalloyed carbon steel used in a collaborative program.

If corrosion product remains on the specimens after the performed degreasing, they are to be removed in the following solutions:

- · diluted hydrochloric acid in case of steel and zinc and
- diluted nitric acid in case of copper.

They are to be subsequently rinsed by running water and then by distilled or deionized water, dried, and weighed.

2.3.4 Handling—After final surface cleaning before exposure, it is important that limited handling occurs. In general, it is necessary to use clean gloves in final handling operations.

2.3.5 Storage—The test specimens before exposure should be stored in a dessicator or sealed into plastic bags with dessicant.

2.3.6 Specimen Data Records-Records include the following:

- chemical composition,
- method of preparation of the test specimens,
- surface cleaning before exposure,
- shape and size, and
- weight.

3. Atmospheric Corrosion Test Sites

The general principles for the selection of the testing localities and their arrangement are mentioned in ISO/DP 8565, Metals and alloys—Atmospheric corrosion testing—General requirements for field tests.

The program also includes the atmospheric test sites, the aggressivity of which is influenced to a great extent, by the level of SO_2 and salinity, that is, the pollution taken into account in the present classification system of ISO.

It is necessary to secure the measurement of the characteristics stated in Table K2.

The aggressivity measurements would necessitate regular monitoring of air temperature, relative humidity, chloride deposition rate, and either sulfur dioxide concentration or sulfur dioxide deposition rate.

For the supplementary program described in the document WG4 N105, further characterization of the environment in terms of NO_x H₂S, NH₃ concentration or deposition rate and dust fallout is sought.

Measured Value	Unit	Types and Number of Measurements	Expression of Results
Air temperature	°C	continuous or at least 3 times per day	average per month and/or per year
Relative Humidity	%	continuous or at least 3 times per day	average per month and/or per year
Air contamination:			
SO ₂ concentration	mg, m^{-3}	continuous monthly	average per month
SO ₂ deposition rate	mg, m^{-2}, d^{-1}	continuous monthly	average per month and year
Cl ⁻ deposition rate	mg, m^{-2}, d^{-1}	continuous monthly	average per month and year

TABLE K2—Environmental factors characterizing atmospheric exposure conditions.

NOTES: (1) Method of the sorption of sulfur dioxide on alkaline surface according to ISO/DP 9225. (2) Method of the sorption of sulfur dioxide on PbO₂ according to ISO/DP 9225. (See ASTM G 91.) (3) For Cl⁻ deposition measurements is the wet-candle method recommended (ISO/DP 9225). (4) For Cl⁻ deposition measurements is also the NILU aerosol-trap (Doc ISO/TC 156/WG4 N124) and the inert catchment plate method as complimentary recommended.

3.1 Exposure Frames

The function of the exposure frames is to maintain test specimens securely in position without themselves undergoing significant deterioration or influencing corrosion of the test specimens attached to them. The frames may be designed to provide full or partial exposure to the weather.

Metal sections or wood may be used, provided that they have adequate strength and durability. If necessary, additional protection can be provided by paint coatings over suitably prepared and primed metal surfaces. Frames may also be constructed from wood suitably protected and maintained.

The practical realization of the following design requirements will depend upon the locally available resources and materials. Frames should be designed to expose as large an area as possible of both the upper and undersides of the specimens. The purpose of this is to enable differences in skyward or groundward exposures to be evaluated, should this be a test requirement. In addition, the structural components of the frame should not shelter the specimens.

The method of attaching specimens to the test frame should prevent neighboring specimens from touching, sheltering, or influencing one another and should also provide complete electrical insulation between the specimens and the test frame. In this latter context, grooved porcelain electrical insulators with fixing holes, or similar devices in inert and durable plastic materials, are suitable. Alternatively, bolts or screws fitted with electrically insulating sleeves and washers, may be used. The area of contact between the test specimens and their holders shall be as small as possible.

The test frames should also be designed to enable specimens to be exposed at an angle of 45° or 30° from horizontal, skyward-facing, or in other orientations required by the test program.

The design of the frame should be such that test specimens are not affected by runoff water from the test frame or other specimens, or by splash water from the ground. The installation of test frames on a site may also cause localized drifting of snow, and therefore some minimum specimen exposure height above ground level may be necessary. This minimum height must be chosen to prevent both splashing by rainwater and burial in snow drifts and should not be less than 0.75 m.

3.2 Test Site Characterization

The environmental data required for the characterization of the atmosphere are as follows:

- air temperature, °C,
- relative humidity, %,
- sulfur dioxide deposition rate, mg, m^{-2} , d^{-1} , or concentration, mg m^{-3} , and
- chloride deposition rate, mg, m⁻², d⁻¹.

The frequency of monitoring these factors is given in Table K2.

Monitoring of the other characteristics complimenting the effect of pollution (dust fallout and rainfall analyses or others) is recommended in an industrial type of atmosphere.

For the supplementary program (see 1.7), further characterization of the environment in terms of NO_x , H_2S , NH_3 , and dust fallout is sought.

3.3 Exposure of Test Specimens

The weighed and marked test specimens shall be placed in such a way that

• contact does not occur either between individual test, specimens, and any material that would affect their corrosion under the test conditions,

• corrosion products and rainwater-containing corrosion products do not drip from the surface of one test specimen to another,

- there is easy access to the surfaces of the test specimens,
- the test specimens are easy to remove,

• the test specimens are protected from falling out, for example, by the action of wind, accidental contamination or destruction,

• all the test specimens are exposed to the same conditions with uniform access of air from all directions,

• the surface of test specimens should, in general, face south in the northern hemisphere and north in the southern hemisphere, but the direction of corrodant source, such as ocean, can be taken into the consideration,

• flat plate specimens are exposed on frames at an angle of 45° or 30° according to the standards in force in the concerned country,

• the helix holders are located on frames so that the helixes are in vertical upright position; this mode of the location secures the attaining of a more uniform rate of corrosion along the entire wire without a differentiation of the bottom and top surfaces, and

• exposure sequences and their scheme (see 1.3 and 1.4)

3.4 Atmospheric Corrosion Test Sites Participated in Collaborative Program ISO CORRAG

Institutions responsible for realization of collaborative program in each participating country are mentioned in Item 6.

Atmospheric corrosion test sites belong also to other national institutions (Norway, Japan, UK, USA, USSR; see Table K3).

4. Method of Test Result Evaluation

4.1 The removal of corrosion products from specimens after exposure is accomplished in accordance with ISO/DP 8407 metals and alloys—procedures for removal of corrosion products from corrosion test specimens.

• Chemical procedures involve exposure of the corrosion test specimen in a specific chemical solution which is designed to remove the corrosion products with minimal dissolution of any base metal.

• Intermittent removal of specimens from the chemical solution for light brushing can often facilitate the removal of lightly adherent corrosion products.

• All cleaning solutions shall be prepared with distilled water and reagent grade chemicals.

• Any cleaning procedure should be followed by a thorough rinsing of the test specimen with distilled water and immediate drying.

• The cleaning procedure should be repeated on specimens several times. The mass loss should be determined after each cleaning by weighing the specimen (weighing to the fifth or sixth significant figure is suggested; see 2.3.3).

• The mass loss should be graphed as function of the number of equal cleaning cycles. The mass loss due to removal of corrosion products will be that corresponding to Point B in Fig. 7. In many cases, the cleaning method will remove all corrosion products during the first cleaning period. The line corresponding to corrosion products removal will not then be obtained. In this case, Point B cannot be obtained, and Point D, obtained by extrapolation to zero cleaning cycles of the metal removal line, may be used.

• Repeated treatment may be required for complete removal of corrosion products. Removal can often be confirmed by examination with a low power microscope, that is, 7X-30X. This is particularly useful with pitted surfaces.

• Chemical cleaning procedures for removal of corrosion products are shown in Table K4.

4.2 Corrosion Rate Calculation

The corrosion rate for each metal, r_{corr} , in μ m/year is calculated according to

$$r_{\rm corr} = \frac{\Delta m}{A\rho t} \times 10$$

where

 $\Delta m = \text{mass loss, mg},$ $A = \text{surface area, cm}^2,$

Country	Designation	Name of Testing Site	Type of Atmosphere
Canada	CND	1. Boucherville	moderate zone, light industrial
CSSR	CS	1. Kasperské Hory	moderate zone, rural
	CS	2. Praha-Bechovice	moderate zone, urban
	CS	3. Kopisty	moderate zone, heavy industrial
FGR	D	1. MPA NRW Dortmund	moderate zone, industrial
Finland	SF	1. Helsinki	moderate zone, urban
	SF	2. Otaniemi	moderate zone, "small town"
_	SF	3. Ahtari	moderate zone, rural
France	F	1. Saint Denia	moderate zone, industrial
	F	2. Ponteau Martigues	moderate zone
	F	3. Picherand	moderate zone, rural
	F	4. Saint Remy Les Landes	moderate zone, marine
	F	5. Salins De Giraud	moderate zone, marine
	F	6. Ostende (belgique)	moderate zone, marine-industrial
	F	7. Paris	moderate zone, urban-industrial
	F	8. Auby	moderate zone, heavy industrial
-	F	9. Biarritz	moderate zone, marine
Japan J 1. Choshi J 2. Negotia suppo		 Choshi (Chiba Prefecture) Negotiations for financial support for two other sites 	moderate zone, urban
		are now underway	
Nomiau	N	3. 1. Osla	moderate zono uchon
Norway	IN N	1. USIO	moderate zone, urban
	IN N	2. Borregaard	moderate zone, industrial
	N	J. DITKENES	range transboundary air pollutants
	N	4. Tannager	moderate zone, marine splash
	Ν	5. Bergen	moderate zone, marine-urban
	Ν	6. Svanwik	cold zone, transboundary air pollutants
Spain	E	1. Madrid	moderate zone, urban
	E	2. El Pardo, Madrid	moderate zone, rural
	E ·	3. Sestao, Bilbao	moderate zone, industrial
	E	4. Puerto de Arriluce, Bilbao	moderate zone, marine
Sweden	S	1. Stockholm-Vanadis	moderate zone, urban
	S	2. Bohus Malmon, Kattesand	moderate zone, marine S2
	S	3. Bohus Malmon, Kvarnvik	moderate zone, marine S3
UK	UK	1. Tinsley, Yorkshire	moderate zone, industrial
	UK	2. Crowthorne, Berkshire	moderate zone, rural
	UK	3. Rye, East Sussex	moderate zone, marine
	UK	4. Fleet Hall, Kent	moderate zone, urban
USA	US	1. Kure Beach, North Carolina	moderate zone, eastern marine
	US	Newark-Kearney, New Jersey	moderate zone, industrial
	US	3. Point Reyes, California	moderate zone, western marine
	US	4. Research Triangle Park, North Carolina	moderate zone, rural
	US	5. Canal Zone, Panama	tropical zone
	US	6. Los Angeles, California	moderate zone, urban
USSR	SU	1. Murmansk	cold zone, marine-rural
	SU	2. Batumi	subtropical, marine-urban
	SU	3. Vladivostok	far east, marine-urban
	SU	4. Jakutsk	cold zone, rural

TABLE K3—Atmospheric corrosion test sites participated in collaborative program ISO CORRAG.



FIG. 7-Mass loss of corroded specimens resulting from repetitive cleaning cycles.

Material	Chemical	Time, min	Temperature, °C	Remarks
Steel	500-mL hydrochloric acid (HCl, sp gr 1.19) 3.5 g hexamethylene tetramine; distilled water to make 1000 mL	10	20 to 25	
Copper	54-mL sulfuric acid (H ₂ SO ₄ , sp gr 1.84); distilled water to make 1000 mL	30 to 60	40 to 50	deaerate solution with nitrogen; brushing of test specimens to remove corrosion products followed by re-immersion for 3 to 4 s is recommended
Aluminum	50-mL phosphoric acid (H ₃ PO ₄ , sp gr 1.69); 20-g chromium trioxide (CrO ₃); distilled water to make 1000 mL	5 to 10	90 to 95	if corrosion product films remain, then follow with nitric acid procedure below
	nitric acid HNO ₃ , sp gr 1.42	1 to 5	20 to 25	remove extraneous deposits and bulky corrosion products to avoid reactions that may result in excessive removal of base metal
Zinc	200-g chromium trioxide (CrO ₃); distilled water to make 1000 mL	1	80	chloride contamination of the chromic acid from corrosion products formed in salt environments should be avoided to prevent attack of the zinc base metal

 TABLE K4—Chemical cleaning procedures for removal of corrosion products.

 $t = \exp$ osure time, years, $\rho = \text{density}, \text{ g/cm}^3,$ $\rho \text{Fe} = 7.86,$ $\rho \text{Cu} = 8.96,$ $\rho \text{Zn} = 7.20, \text{ and}$ $\rho \text{AI} = 2.70.$

The corrosion rate for open helix specimen in micrometres per year $(\mu m/y)$, can be calculated according to

$$r_{\rm corr} = 0.25 \, \frac{\Delta m d}{m t}$$

where

 $\Delta m = \text{mass loss, mg,}$ d = wire diameter, mm, m = original mass, g, andt = exposure time, years.

NOTE: In cases where $\Delta m/m$ exceeds 50 use

$$r_{\rm corr} = \frac{1000 d}{2t} \left[1 - \left(1 - \frac{\Delta m}{1000 m} \right)^{1/2} \right]$$

In the test report, all single values and the mean values have to be represented.

4.3 Evaluation of Local Corrosion of Aluminum

After removal of the corrosion products (see 4.1), the local attack of aluminum is evaluated on flat specimens either by the following procedures or according to ASTM Recommended Practice for Examination and Evaluation of Pitting Corrosion (G 46).

4.3.1 Determination of Area with Local Corrosion Attack—The wire screen of flexible transparent material with squares of 5 by 5 mm is used for the evaluation and the area with local corrosion attack (%) is calculated according to the following formula

$$P(\%) = \frac{100}{n \cdot N}$$

where

n = number of squares with local attack and

N =total number of squares.

NOTE: The top and lower side of the specimen shall be evaluated separately.

4.3.2 Determination of Local Penetration Depth—The following methods are to be used for the determination of the local penetration depth:

- by measuring microscope,
- by needle indicator, or
- by metallographic method on cross section.

At least 20 points are to be measured (p_i in μ m). The results are to be statistically processed, for example, according to ASTM G 46 or Recommended Practice for Applying Statistics to Analysis Corrosion Data (G 16) or both and the following values are expressed:

 $p_{\text{mean}} = \text{mean depth of local attack (pits) and}$

 p_{extr} = extreme value of local penetration calculated by the method of the statistics of extreme values (for a normal distribution of the set of results $p_{\text{extr}} = p_{\text{mean}} + 3 \times \text{standard deviation}$).

5. Methods of Data Processing

5.1 Environmental Data

The environmental data have been processed in the form of annual surveys into tables according to the form (Table K5). In case that further characteristics of the environment are followed (see 3.2), they are processed into individual tables in the same mode.

5.2 Results of Corrosion Tests

5.2.1 One-Year Exposures—The results of the one-year exposure (exposure sequences 11, 12, 13, 14, 15, 16) are processed into tables according to the form (see Table K6)

The results of the supplementary program, if exposed (see 1.7), are processed into individual tables in the same mode.

5.2.2 Long-Term Exposures—The results of the long-term exposures (exposure sequences 21, 41, \times 1) are processed into tables according to the form (see Table K7).

The results of the supplementary program, if exposed (see 1.7), are processed into individual tables in the same mode.

5.2.3 Local Corrosion of Aluminum—The results of the evaluation of the local corrosion of aluminum (see 4.3.1 and 4.3.2) for all exposure sequences are processed into a table according to the form (see Table K8).

It is recommended to present to complementary environmental characteristics (rainfall analyses, dust fallout) in a similar manner.

NOTE: (1) Minimum and maximum values should be reported. (2) It is also possible to express time of wetness as hours with relative humidity above 80%. (3) Recommended measurement: it is necessary to indicate the system of measurement.

5.3 The Handing Over and Analysis of Results

The results of the collaborative testing program will be utilized for further work of WG4 and also their collaborative utilization in the form of lectures or publications is assumed.

The results of the evaluations of the samples taking off after 1, 2, and 4 years and the annual surveys of the atmospheric environment characteristics (see 5.1 and 5.2) are to be sent to the Secretariat of WG4 which will summarize the concerned results and send them to all participant members of WG4.

The analysis of the results is carried out after 2 and 4 years of exposure.

A collective calculation as well as a theoretical and technical processing of the results will be carried out after the evaluation of four years of exposure. The mode of the processing, as well as the distribution of tasks among the partners, will be stipulated on the basis of the analysis of results after two years of exposure.

The basic terms and tasks are evident of the working schedule in the enclosure. The progress of work will be regularly evaluated during the consultations on work of WG4 where also possible modifications and amendments will be decided.

List of Participants

Participated institutions, contacts, and addresses are listed in Table K9.
		Measured Time of Wetnes (hrs)														
nmental data.		Calculated	80%, h (hrs)													
		stic		dep. (mg, m^{-2}, d^{-1})												
urvey of environ	Code:	Environmental Characteristi	Environmental Characteris SO ₂	conc. (mg, m ⁻³)												
TABLE K5—Yearly				dep. (mg, m^{-2}, d^{-1})												
				Humidity (%)												
				Temperature (°C)												
	Test Site: Country: Year:			Month	01	02	03	0 5	90	07	80	60	10	11	12	C

of environmental data. i Vacato

TABLE K6–Results of one-year exposure.

Test Site: Country: Year:					Code:					
			clat Specimens					lelix Specimer	SI	
Jo of			Corrosion R	ate (μm/y)		Ĩ		Corrosion I	Rate (μm/y)	
Exposure	from/to	Steel	Zinc	Copper	Aluminum	from/to	Steel	Zinc	Copper	Aluminum
11		1.								
		2.					2.			
		З.					З.			
		0					0			
12		1 .					1.			
		2.					2.			
		з.					З.			
		0					0			
The same fo	orm for exposu	res 13-16.								

TABLE K7-Results of long-term exposure.

Test Site: Country: Year:					Code:					
			Flat Specimens					Helix Specime	su	
2			Corrosion R	late (μm/y)		L		Corrosion	Rate (μm/y)	
No. of Exposure	Exposure - from/to	Steel	Zinc	Copper	Aluminum	from/to	Steel	Zinc	Copper	Aluminum
		2	Years Exposur	e			2	Years Exposu	Ire	
21		0.3.2.1					1. 0.3.2.1			
		4	Years Exposur	e						
41										
The same fo	rm for Exposu	re X1.								

TABLE K8—Results of evaluation of local attack of aluminum.

Test Site: Country:			Code:				
				Flat Sp	ecimens		
					Pit dep	th (μm)	
No. of	European	Area (%)		P _{mean}		P,	extr
Exposure	from/to	A ^a	B ^a	Aª	Ba	A ^a	Bª
11							
12							
13							
14							
15							
16							
21							
41							
X1							

"A is top side of specimen and B is lower side of specimen.

Country	Institution	Contact	Address
Canada	National Research Council, Industrial Materials Research Institute	J. J. Hechler	75 de Mortagne Blvd. Boucherville, Quebec CANADA J4B 6Y4
CSSR	State Research Institute for Protection of Materials	P. Holler	Praha 9—Bechovice 250 97 CZECHOSLOVAKIA
FGR	Staatliches Materialprüfungsamt N.W.	C. L. Kruse	Marsbruchstrasse 186 D-4600 Dortmund 41 BRD
Finland	Technical Research Centre of Finland (VTT) Metallurgy Laboratory	T. Hakkarainen	Metallimiehenkuja 4 SF-02150 Espoo FINLAND
France	EDF-DER Département ENA	M. Legrand (atm test sites Nos. 1-4)	Les Renardiéres Route de seus 77250 Ecuelles FRANCE
	Cegedur Pechiney	M. Reboul (atm test sites Nos. 5-7)	BP 27 38340 Voreppe FRANCE
	Centre Technique du Zinc	M. Piessen (atm test site No. 8)	34 rue de Collange 92307 Levallois Perret FRANCE
	IRSID Institut de la Recherche la Sidèrergie Française	M. Jossic (atm test site No. 9)	185 rue du Président Roosevelt 78105 St Germaín en Laye FRANCE
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Spain	Centro Nacional de Investigaciones Metalurgicas	M. Morcillo	Avenida de Gregoria del Amo Ciudad Universitaria Madrid 3 ESPANA
Sweden	Swedish Corrosion Institute	J. Gullman	Box 5607 S-11486 Stockholm SWEDEN
UK	Central Electricity Research Laboratories	P. McIntyre	Kelvin Avenue Leatherhead Surrey KT22 7SE GREAT BRITAIN
USA	Air Products & Chemicals, Inc.	S. W. Dean	Allentown, PA 18195 USA
USSR	IFCHAN SSSR	P. V. Strekalov	Leninsky prospekt 31 117 312 Moscow USSR

TABLE K9-List of participants.

Summary

The 25 papers that are included in this STP provide a representative cross section of the recent international interest and activity in corrosion of materials in atmospheric environments. The subject matter of the individual papers lend themselves to categorization in the areas of

- materials performance,
- environment characterization, and
- test methods.

The principal focus of each paper dictated the broad category into which it has been placed. However, many papers include information on all three categories of materials performance, environment characterizations, and test methodologies. The reader therefore is encouraged to survey all groups of papers in the search for information on a particular subject category.

Materials Performance

The papers on characterization and documentation of materials performance encompass most major structural or architectural metals used in atmospheric applications. Articles by Shastry et al. and Raman deal with performance of weathering steels in a variety of atmospheric environments and discuss environmental conditions under which varying degrees of corrosion performance have been noted. Cleary summarizes results of industrial atmospheric tests to assess the benefits of a chromate passivation treatment on performance of Al-Zn coated sheet steel.

Three papers deal with performance of stainless steel alloys including one by Johnson et al. summarizing corrosion behavior of several alloys in various environmental applications. The paper by Baker and Lee reports results of a long-term marine atmosphere test of several stainless steels conducted by ASTM at several of its standard atmospheric test sites. Ito et al. summarize a test program on stainless steels that characterizes materials performance and environmental effects, outlines a new laboratory test method, and summarizes results of an alloy development program.

Materials performance in specific applications are presented in papers by Eiselstein and Caligiuri on high carbon steel in bridge suspension cables, Fishman on performance of architectural copper after up to 100-years exposure at Yale University, and Lee et al. on several materials used in telecommunications hardware in Canada.

The final group of materials performance papers include one by Baker and Morton on marine atmospheric exposures of eight classes of metals for periods from 23 to over 45 years. The paper by Baboian and Haynes summarizes results of 15-year tests at several test locations documenting behavior of a wide range of clad metal combinations. Dean and Anthony report on corrosion behavior of several wrought aluminum alloys exposed in an unstressed condition at three test sites for 10 years. The paper by Shaw and Aylor summarizes marine atmospheric test results for a variety of metallic, ceramic, and metallic/ceramic coatings on aluminum and steel alloys.

Environment Characterizations

A group of eight papers principally focus on assessing the effects of environmental factors on performance of materials and on the general characterization of relative environment corrosivi-

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ties. Cramer et al. summarize results of a test program within the National Acid Precipitation Assessment Program to measure the corrosion behavior of structural metals and the incremental effects of acidic deposition. The paper by Vrobel and Knotkova describes a system of classifying relative corrosivity of geographic locations within Czechoslovakia for the purpose of enhancing service lives of structures and products. Kucera et al. also describe a system of classifying corrosivity of atmospheres based on tests at a number of sites in Scandinavia.

Haynie describes the results of a field study on galvanized steel performance in which environmental monitoring data provides a basis for characterizing relative environmental "cause" and corrosion "effect." In a similar vein, Franey summarizes laboratory tests in which effects of specific atmospheric trace gases are assessed on corrosion behavior of copper and copper alloys.

The paper by Knotkova and Tu reports laboratory test results designed to assess the combined effects of industrial and marine environments on corrosion. Duncan and Ballance also report on effects of marine atmospheres in their field studies designed to determine the extent of sea-salt influence on corrosion at sites inland from the coast. The paper by Graedel addresses the basic understandings of atmospheric chemistries and the potential effects of various environmental parameters on corrosion.

Test Methods

Methods for assessing corrosion behavior of materials are the principal focus of the final group of papers in this STP. Spence describes results of a test methodology designed to establish the relative effects of dry and wet deposition on corrosion of structural materials. Agarwala summarizes a corrosion monitoring test method for determining the corrosivity of naval environments. Ito et al. report on a test method to measure the relative protectiveness of rust films on weathering steel structures. The paper by Schubert describes the results of test using an accelerated test method designed to control and monitor critical parameters,

Sheldon W. Dean

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National Association of Corrosion Engineers, Houston, TX 77218; symposium cochairman and coeditors.

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