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INFLUENCE OF MARINE ORGANISMS ON THE
LIFE OF STRUCTURAL STEELS IN SEAWATER

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The controlling influence of biological activity is indicated by the results of NRL's 16-yr corrosion investigation in Panama. The long-term data reveal the protective effect of fouling against normal corrosion and the development of constant-rate bacterial corrosion. Furthermore, the results suggest that selective control of marine bacteria could be the key to achieving very low corrosion rates of structural steels in seawater.

To investigate these effects in different climates and with different organisms present, racks of carbon steel specimens were immersed at five ocean locations. At all sites, after sufficient fouling collected, bacterial corrosion became the dominant type over most of the specimens. At that point corrosion rates stabilized to a constant value. These steady-state rates were found to be lower than expected and surprisingly uniform for the different marine environments, ranging from ~~2- to~~ 3-mils per year.

Results from these NRL studies have been combined with data from other ocean exposure studies to establish a procedure for estimating steel corrosion loss in temperate or tropical seawater for any desired period of exposure.

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INFLUENCE OF MARINE ORGANISMS ON THE LIFE OF STRUCTURAL STEELS IN SEAWATER

INTRODUCTION

Structural carbon steel is one of the most useful and widely used construction materials. Its combination of high strength, formability, weldability, and relative economy of use is unmatched by other materials. As a result, the tonnage of steel produced far overbalances the total tonnage for all other construction metals. It is used widely in the marine environment for ship hulls, buoys, containers, retaining walls, piles, and underwater construction members of all types. Its biggest drawback for marine use is its susceptibility to corrosion in the saline environment.

The cost of protecting steel from marine corrosion is staggering. Part of this expenditure may be unnecessary. Two of the reasons for this overprotection are that steel corrosion is voluminous and ugly, giving the appearance of great damage, and that actual corrosion rates of this material over extended periods are relatively unknown. Corrosion rates reported in the literature are usually obtained from short-term tests averaged over the entire period of exposure, starting from zero time; however, marine corrosion of carbon steel normally proceeds very rapidly initially and then levels off to a linear relationship. This steady-state rate for the linear portion of the corrosion-vs-time curve is the most important value for estimating the service life of a steel structure in seawater. Another factor in overprotection is the little-understood effect of biological activity on the corrosion rates. Ferrous metals are probably more affected by marine organisms than any other class of metal, yet these biological influences have been practically ignored by corrosion scientists. Classical treatises on corrosion usually disregard the biological impact or mention it only as a minor or isolated effect.

Because of the extensive use of steels in marine structures, the corrosion rates of these metals in different seawaters and the effects of different marine organisms on their corrosion rates are of great interest to the Navy. This report will analyze the roles certain marine organisms play in controlling steel corrosion, establish the steady-state rates for carbon steel in different seawater environments between 9°N and 51°N latitude, and develop methods for using these rates for estimating losses over extended exposure periods.

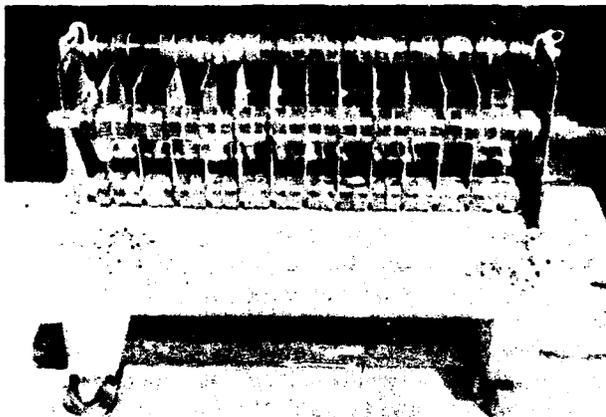
ANALYSIS OF DATA FROM LONG-TERM EXPOSURES

A 16-year study of the corrosion rates of a large number of metals exposed in the Pacific Ocean at Naos Island, Panama C.Z., and in other tropical aqueous and atmospheric environments has been completed by NRL (1-4). The metal most intensively investigated in this study was structural carbon steel (AISI 1020). Long-term corrosion-vs-time relations for this metal in tropical seawater were established at the Naos Island site. These

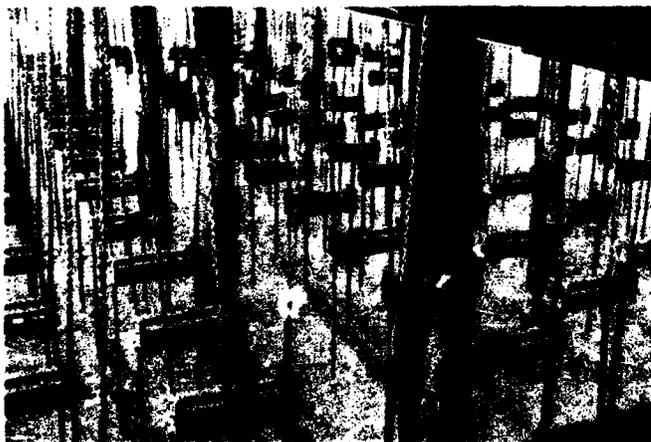
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relationships were determined by exposing 30 steel replicates and removing six of these at 1, 2, 4, 8, and 16 years. Weight loss, pit depths, and tensile strength changes were measured for each panel (1), and observations were made on the amount and types of fouling and corrosion products. Similarly, 30-set arrays were exposed at mean-tide elevation at Naos Island and in the fresh water of Gatun Lake, Canal Zone. Figure 1 shows a view of the test specimens on exposure at the Naos Island pier. A few panels were also immersed in the ($<1\text{‰}$) brackish water of Miraflores Lake, Canal Zone. The corrosion rates obtained and the biological activity observed for the four different environments provide interesting insights into the true corrosion rates of steel in aqueous environments and the important influence of marine organisms on corrosion in seawater.



(a)



(b)

Fig. 1—Long-term corrosion specimens exposed in Pacific seawater at Naos Island, Canal Zone (a) Closeup of immersion rack with specimens in place (b) View of test pier at low tide with mean-tide racks visible

Comparison of Four Aqueous Environments

In the four environments described above (three continuous immersions and one mean tide) the corrosion differences for carbon steel are considerable. Corrosion vs time curves are shown for the three underwater exposures in Fig. 2. In continuous seawater immersion at Naos Island all panels were completely covered within a year by hard fouling organisms, predominantly encrusting bryozoa. At subsequent removals it was observed that the buildup on the metal consisted of three distinct layers: the top layer was an essentially continuous fouling cover; the second layer was comprised of hard corrosion scale, and finally, next to the metal surface, there was a continuous layer of a soft black corrosion product, rich in sulfides.

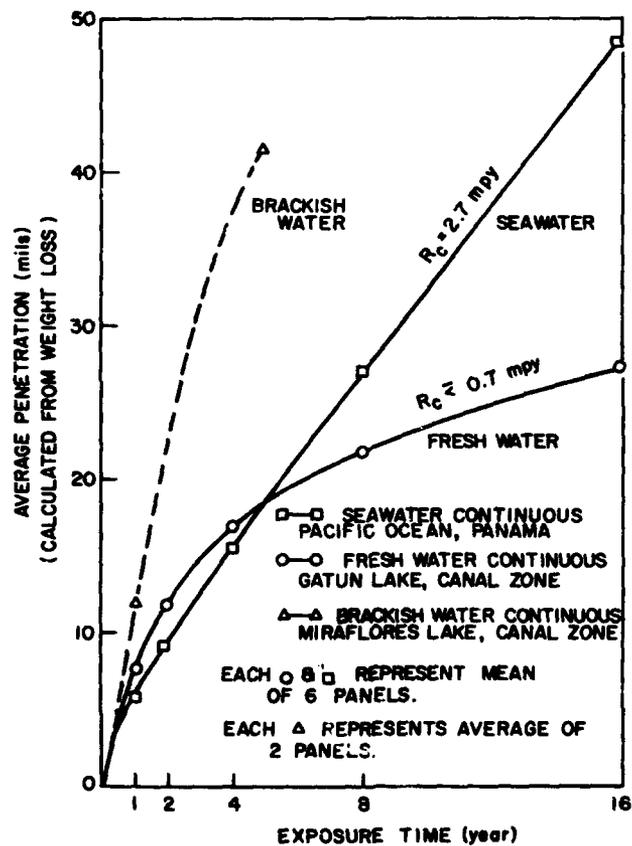


Fig. 2—Corrosion-vs-time curves for carbon steel in three different aqueous environments

On the specimens exposed at mean tide, fouling did not develop as rapidly; however, at between 1 and 2 yr a complete calcareous cover of barnacles had become attached, and subsequently the sulfide-containing layer was formed next to the metal. In the fresh and mildly brackish water no hard fouling collected, and heavy sulfide deposits were not observed.

Oxygen Diffusion Control in Fresh Water

From the curve in Fig. 2 and the visual observations of the panels it was determined that in fresh water, with no marine biological activity, the steel sustained high initial weight losses followed by an ever-decreasing corrosion rate. A linear corrosion-vs-time relation was approached only after 8 yr, at which time the rate had dropped to less than 1 mpy.* Since the corrosion rate is normally controlled by the amount of oxygen available for depolarization of cathodic areas, such a relation indicates that the constantly increasing film of corrosion products caused a continuing reduction in oxygen diffusion to the metal surface, and a parabolic time-vs-corrosion relation resulted.

Biological Control in Marine Environments

In the much more corrosive seawater medium, the corrosion rate seemed to be modified and regulated by the action and interaction of marine fouling macroorganisms and marine bacteria. The steel panels continuously immersed in seawater corroded very rapidly at first, but they quickly developed a fouling cover which then provided appreciable protection to the metal. Without fouling, the seawater would undoubtedly have produced the highest corrosion losses of any of the four environments; this is indicated by comparison of the brackish water and seawater curves in Fig. 2, as well as the two curves from the Caribbean Sea to be discussed later. The slightly brackish water could not sustain marine fouling, and the absence of fouling was conducive to increased corrosion, overbalancing the opposing corrosion-reducing effect of low salinity. The result was a much higher 4 yr corrosion loss for the brackish water specimens than for the seawater panels protected by fouling.

The seawater curve in Fig. 2 is practically linear after the first year of exposure. Such a linear relation would be improbable if the corrosion were being controlled by the diffusion of oxygen through a continually thickening corrosion scale and fouling cover; another explanation was therefore sought. With the long-term data available for study we were able to postulate that some time before the first measurement, at one year, the combined corrosion scale and fouling cover reached sufficient thickness to form an effective barrier against oxygen diffusion to the corroding surface. The exclusion of oxygen from the metal surface is probably not entirely dependent on the impermeability of the fouling cover, since as a consequence of their respiration, aerobic saprophytic bacteria present in the outer fouling layers may also contribute by intercepting some or all of the inward-moving oxygen. This possible protective role of these organisms has been discussed in the literature (5,6).

*Average penetration, mils per year.

When conditions become such that little or no oxygen reaches the metal surface, the corrosion rate should drop to a very low value. No such drop was detected in the Naos Island immersion exposures; however, the fouling developed very rapidly at this site, and it is possible that a dip in the rate occurred sometime before the first measurement at one year.

The low rate did not continue, however, because of the activity of anaerobic sulfate-reducing bacteria on the metal surfaces. These bacteria of the genus *Desulfovibrio* were first recognized as important in soil corrosion by the Dutch researchers van der Vlugt and von Wolzogen Kuhr (7). Their theory on microbial corrosion by *Desulfovibrio* provided for the removal by these organisms of hydrogen adsorbed on cathodic surface areas, thereby causing cathodic depolarization and continuing solution of metal ions in anodic areas. Aerobic depolarization results from an inward diffusion of oxygen to the corroding surface where it combines with the hydrogen to form water. In anaerobic environments, according to the Dutch hypothesis, this reaction is transferred to the sulfate-reducing bacteria which utilize the hydrogen to reduce sulfate to sulfide. This material then reacts with ferrous ions to form FeS. This theory has been strengthened by later studies (8,9). On the other hand, subsequent investigations (10,11) have indicated that sulfide byproducts of bacterial metabolism acting either directly or galvanically are more important. Although the true bacterial corrosion process still remains to be fully understood, there is general agreement that for appreciable corrosion to occur from sulfate-reducing bacteria, the following conditions must exist: (a) an absence of oxygen, (b) a source of sulfates, (c) a source of organic nutrients, and (d) the presence of ferrous ions (12).

After buildup of the oxygen-excluding cover of fouling, corrosion scale, and possibly marine slime, an anaerobic environment develops at the metal surface. This provides the final necessary condition requisite for the growth of sulfate-reducing bacteria. The other requirements are satisfied in normal seawater by the presence of ferrous ions from the metal, sulfate from the water, and a nutrient supply from the decomposing fouling organisms. Once these environmental conditions are established, the corrosion, which has been slowed by the natural protective fouling and corrosion scale cover, increases and approaches a constant rate which remains independent of further thickening of the cover. The seawater curve in Fig. 2 shows that at Naos Island the steady-state rate for average penetration of carbon steel was 2.7 mpy. This value was approached after the first year and continued virtually unchanged through the 16 years of exposure.

When the corrosion losses were plotted against time for the mean-tide panels, some interesting results were revealed which seemed to contribute significantly to a biological control theory of marine corrosion. Figure 3 presents the curve for these mean-tide data. It can be seen that corrosion loss was very high during the first year (10 mpy)—almost double that found for continuous immersion. Fouling, mostly barnacles, collected on these panels, but at a much slower rate than for the continuously immersed specimens nearby. Only after a year of exposure did the mean-tide fouling become sufficiently dense to provide a high degree of protection to the metal. Because of this protection the corrosion rate during the exposure interval between 1 and 2 yr dropped to a very low value of less than 0.5 mpy. Conditions of a slower fouling buildup and a higher oxygen availability at mean-tide elevation probably delayed the development of completely anaerobic conditions at the metal surface; this evidently resulted in an extension of the period of protection by fouling. If bacterial growth could be inhibited at this point, the corrosion rate should remain very low, and as in the case of weathering steel in the atmosphere,

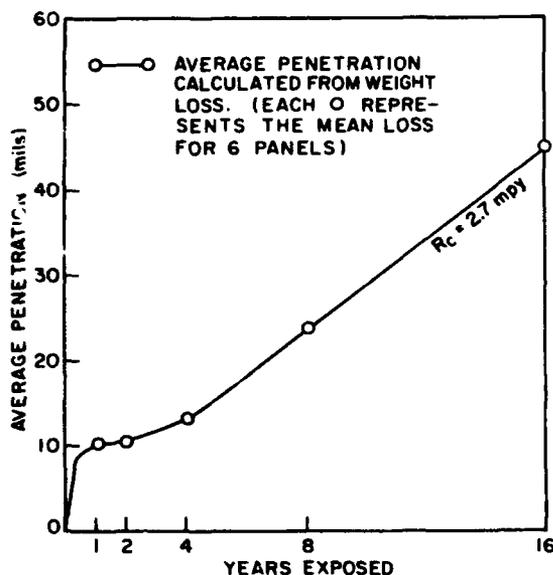


Fig. 3—Corrosion-vs-time curve for carbon steel exposed at a mean-tide elevation

in which many years of service are obtained with little or no maintenance, long-term marine durability of uncoated structural steels should be attainable.

Eventually anaerobic bacterial activity did develop on the specimens at mean tide, and after 4 yr reached a degree equal to that of continuous immersion. The final corrosion rate between 4 and 16 years' exposure was constant and exactly the same as the steady-state rate of 2.7 mpy for the continuously immersed panels.

In addition to carbon steel, other structural ferrous metals were included in the Naos Island exposures; these included eight low-alloy steels, a machined cast steel, and an Aston process wrought iron. With the exception of the low-alloy steels containing chromium,* all fell within the range of 2.4–2.7 mpy for the final steady-state corrosion rate.

Most of the discussion so far has been limited to general surface corrosion (average penetration) determined by specimen weight loss. In carbon steel this is directly related to tensile strength reduction and is thus a good indicator of structural strength loss. However, where perforation of a structure or container is the major concern, pitting penetration becomes an important consideration. The effect of biological activity on pitting rates is therefore of considerable interest. Some of the data from the long-term studies provide insight into bio-pitting. Curves for cast and wrought carbon steel for pitting and weight loss are shown in Fig. 4. It can be seen that the average pitting penetration starts at a much higher rate than the weight loss; by the end of two years the average of the deepest pits is 5 to 7 times the depth of the average penetration based on weight loss. After the second year of exposure, however, pitting also appears to be controlled by

*Chromium steels showed lower initial but higher final rates (1).

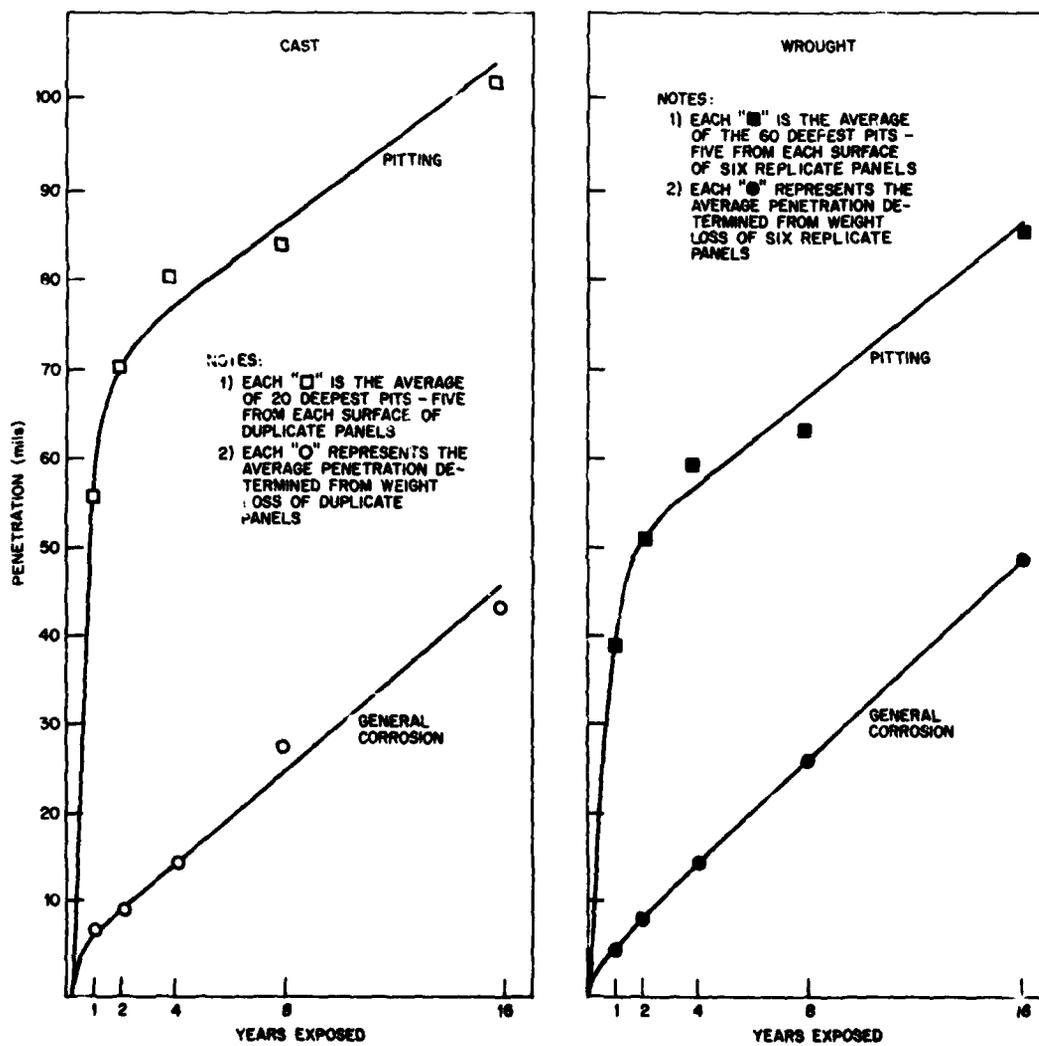


Fig. 4--Curves showing weight-loss and pitting for (a) cast steel and (b) wrought carbon steel continuously immersed in seawater

marine organisms; between 2 and 16 years the average pitting curve is linear and approximately parallels the general corrosion curve at 2.5-2.7 mpy. This seems to indicate that once closed-system, anaerobic corrosion conditions are established, the normal pitting potential patterns are eliminated and corrosion by bacterial activity proceeds uniformly over the entire surface.

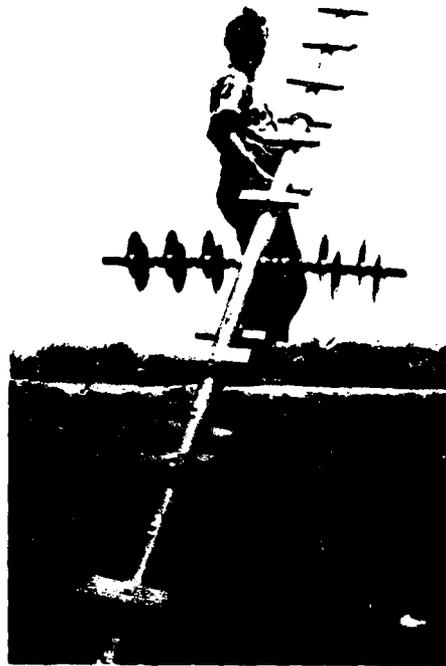
CURRENT CORROSION STUDIES AT FIVE OCEAN SITES

By the end of these long-term studies it was known that at the Naos Island site fouling was acting as an oxygen-shielding, self-healing protective covering, and that sulfate-reducing bacteria were active over the entire panel surfaces. However, it had not been determined when this shielding became effective, when the anaerobic bacteria took control of the corrosion process, or how these events related to the final linearity of the curves. Furthermore, all the long-term seawater data were based on exposures at one site only, where encrusting bryozoa were the principal fouling organisms. Completely unknown were the effects of different ocean locations and whether the anaerobic bacteria could become established and dominate the corrosion process under other types of fouling and in waters of different temperature and salinity. Neither was it known how other types of fouling would affect the corrosion rates.

When NRL personnel initiated a biological deterioration survey at several ocean exposure sites in 1969-70, it was decided to establish the corrosion rate of structural steel at each of these sites and to investigate further the bio-control theory of marine corrosion. Racks containing 12-14 carbon steel disks, all cut from the same sheet of metal, were immersed at five different marine sites. All racks were suspended 6 ft above the bottom in seawater averaging 12-18 ft deep at mean low tide. The first biological evaluation rack containing a steel specimen rack was installed at Naos Island at the same Pacific-side location used for the original long-term corrosion studies. This array was followed by one on the Caribbean coast of the Isthmus of Panama, at the Coco Solo Naval Station on Manzanillo Bay, an arm of the Caribbean. A view of the Caribbean bio-evaluation rack with wood and metal specimens attached, is shown in Fig. 5. Subsequently, arrays were exposed at the Patuxent River Naval Air Station on Chesapeake Bay; at NRL's Marine Corrosion Laboratory at Fleming Key, Key West, Florida; and in St. Andrew Bay, Gulf of Mexico, at the Naval Coastal Systems Laboratory at Panama City, Florida. Two specimens from each rack were removed at six or seven different time intervals, beginning with some early removals at less than one month. From these duplicate specimens the average corrosion penetration was determined by weight loss, and the weight and type of marine fouling were established. Finally, the onset and extent of sulfate-reducing bacterial activity were evaluated by inoculating Sulfate API Broth (specific for sulfate-reducing bacteria) with material from the soft, black corrosion layer found next to the metal and by testing for the presence of sulfide in this layer by hydrogen sulfide generation, using lead acetate paper as an indicator.

So that exposure results could be correlated with the earlier 16-yr data, the same carbon steel (AISI 1020) was used, and although panels were shaped differently for the two exposures, the same edge-to-area ratio (0.056) was maintained; also, the same procedures were used for preexposure pickling to remove mill scale and for postexposure cleaning to remove fouling and corrosion products (1).

Fig. 5—Steel disks mounted on crossarm of biological evaluation staff ready for immersion in Manzanillo Bay, Coco Solo, Canal Zone



Since the exposures at the five sites were not started simultaneously, sufficient time has not elapsed to permit the establishment of final corrosion curves for all locations. The longest-term data, 2.5 years, have been obtained at Naos Island, where by the first 3 to 6 months the samples were covered with a complete coating of encrusting bryozoans. The first point of interest from these repeat exposures at this site is a comparison of the two sets of data collected 20 yr apart. Figure 6 shows the corrosion-vs-time relation for the current exposure series at Naos Island compared with the first portion of the curve for the original long-term data collected at the same site. The agreement is quite good, and the best-fit lines indicate that the steady-state rate for the current exposures is also about 3 mpy, as it was 20 yr earlier.

In the current study at Naos Island, specimens removed in less than 1 yr reveal very high initial corrosion rates, up to 16 mpy (80 mdd)* at 21 days. However, the curve dips appreciably between 6 and 12 months, and the corrosion rate is slowed to less than 1.5 mpy. As with the more pronounced corrosion drop in the original mean-tide exposures, this dip may represent a period of fouling protection prior to the full-scale development of a sulfate-reducing bacterial population. However, this transient attenuation in corrosion rate was not as pronounced at the other four underwater test sites in the current exposures.

*Milligrams per square decimeter per day.

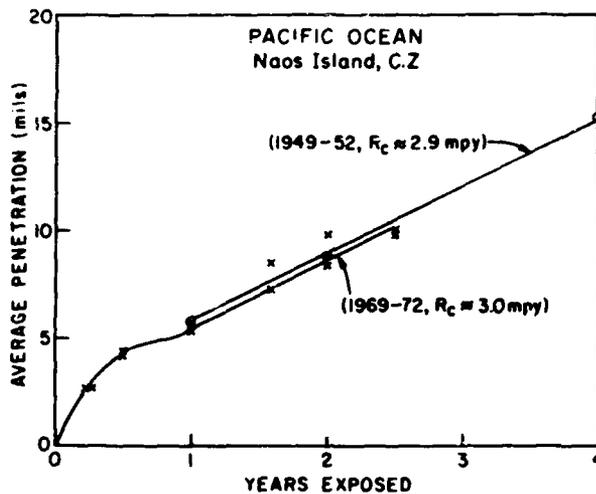


Fig. 6—Comparison of corrosion curves for carbon steel immersed in the Pacific Ocean at Naos Island, C.Z. in 1949 and at the same location in 1969

Protective Effects of Marine Fouling

Although extensive marine borer and fouling studies have been made on the Caribbean side of Panama in Manzanillo Bay at Coco Solo, the corrosiveness of the water at this site had not been previously determined. The water temperature averages about 1°C higher than at Naos Island and the oxygen content is also slightly higher, so the corrosion rate should be as great or a little greater. However, the fouling which consists primarily of barnacles is normally extremely heavy, accumulating a mass of approximately 62 g/dm^2 in three months. Probably because of this rapid and heavy accumulation of barnacles, the first-year corrosion loss was only about $2/3$ of the first-year loss at Naos Island. Figure 7 shows a comparison of the 1-yr fouling attachment at the two sites.

Corrosion curves for heavy and light fouling attachment at a single site (Caribbean, Coco Solo) are presented in Fig. 8. The lower curve represents normal fouling conditions at Coco Solo. The protective fouling developed very rapidly, and at 3 months it appears that the corrosion had already changed to a bacterial process. A steady-state rate of about 3 mpy had been established. The upper curve is the result of an unusual and fortunate set of circumstances. Coco Solo harbor had been in use as a test site for over 10 yr and the water had always produced an extremely heavy barnacle attachment, but during this current test period something drastically inhibited the barnacle population. The reason for the sudden decrease in barnacles has not been established, although it is possible that weed killers used in clearing drainage channels emptying into the harbor may have been the cause. When this decrease in fouling was noted, a second rack of steel specimens was immersed at the Coco Solo site. The upper curve is for this second, lightly fouled set of specimens. A comparison of the two curves gives us the best insight we have yet obtained into the protective effects of marine fouling. They show the difference in seawater corrosion at a specific location when the amount of fouling cover

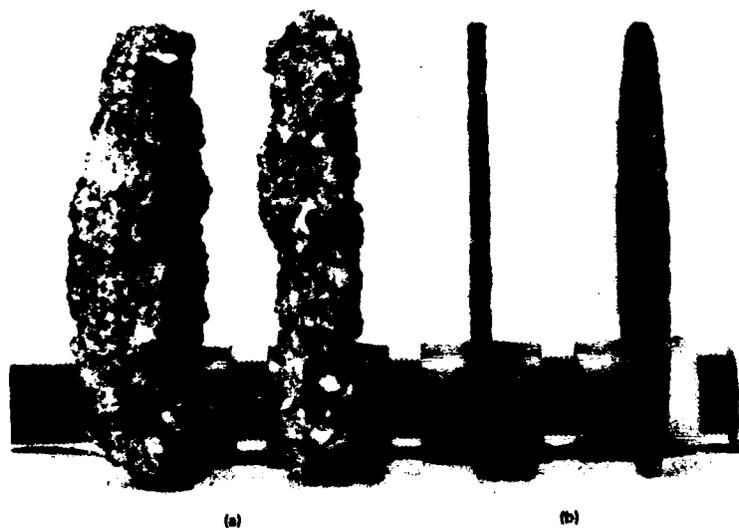


Fig. 7—Fouling accumulation on steel specimens exposed simultaneously for 1 yr in (a) the Caribbean Sea at Coco Solo, C.Z., and (b) the Pacific Ocean at Naos Island, C.Z.

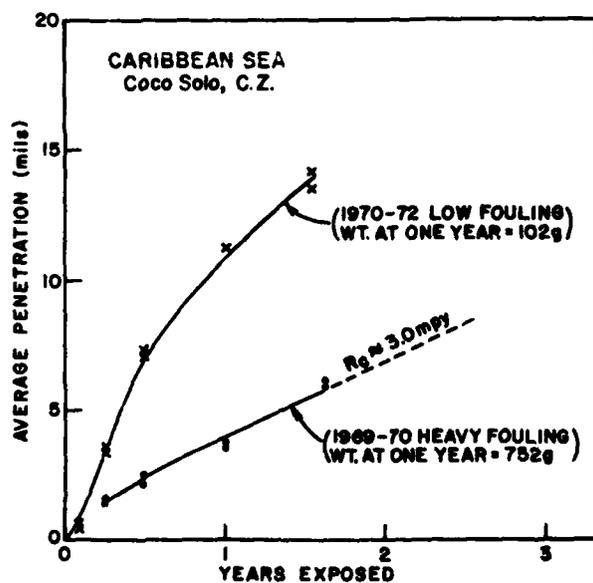


Fig. 8—Corrosion-time curves for carbon steel in Caribbean seawater at Coco Solo, C.Z. showing the protective effect of a heavy fouling cover

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was reduced about 85%. At 1 yr the corrosion loss was over 3 times as great for the rack with low fouling.

With the data presented from these current studies combined with those from the earlier long-term exposures, it becomes evident that complete covers of marine fouling can be useful in reducing steel corrosion. The fact that anaerobic conditions developed at all metal surfaces indicated the effectiveness of the different types of fouling in preventing oxygen from reaching the metal surface and scavenging hydrogen. Development of methods for assuring a heavy fouling cover on stationary marine structures is a desirable research goal. Crisp and Meadows (13) have shown that barnacles can be attracted to surfaces treated with barnacle extracts. In one instance an order of magnitude increase in settlement was obtained. Such methods may have practical applications in the treatment of steel surfaces and should be investigated for this purpose.

Comparative corrosion and biological data for all of the five test locations during the first year of exposure are shown in Table 1. At the two temperate-climate sites, Chesapeake Bay near the Patuxent River and St. Andrew Bay on the Gulf of Mexico, the panels were not completely covered with macro-fouling during most of the first year of exposure. At both of these sites a variety of organisms was present, with the predominant forms being algae and barnacles in Chesapeake Bay and algae, oysters, and tunicates in St. Andrew Bay. Although seasonal temperature changes and growing cycles at these two temperate-water sites exert a masking influence on the short-term data available, the fouling at these two locations also seems to provide considerable early corrosion protection to the steel surfaces.

At Key West, Florida different fouling prevailed; there the specimens rapidly collected a thick coating of plants, principally algae of the genus *Enteromorpha*. Very little

Table 1
Biological Activity and Corrosion at Different Marine Exposure Sites

Location	Average Salinity (ppt)	Year Exposed	Fouling	Weight of Fouling Attachment at 1 yr (g/dm ²)	Metal Weight Loss at 1 yr (g/dm ²)	Sulphate-Reducing Bacteria at 1 yr
Panama Pacific Naos Is., C.Z.	30	1969	Encrusting Bryozoa	16	10.6	Very heavy
Panama Caribbean Coco Solo, C.Z.	31	1969	Very heavy barnacles	90	7.3	Very heavy
Chesapeake Bay Patuxent NATC	18	1969	Algae and barnacles	19	7.2	Moderate
St. Andrew Bay Panama City, Fla.	26	1971	Scattered oysters & tunicates	53	11.0	Moderate
Fleming Key Key West, Fla.	37	1970	Very heavy algae (<i>Enteromorpha</i>)	15	7.4	Heavy

calcareous fouling was observed at this site. Probably because of its more rapid development, this vegetable fouling provided the most effective early protection to the steel. The high initial corrosion loss normal for most seawater sites was not in evidence at Key West; for example, the average rate through the first 90 days was only 22 mdd, compared with 55 mdd at Naos Island. However, the final steady-state corrosion rate at Key West also seems to be controlled by sulfate-reducing bacteria and falls into the same 2-3 mpy range normal for the four other sites.

Distribution and Influence of Sulfate-Reducing Bacteria

Most previous studies of corrosion by sulfate-reducing bacteria have been directed toward soil-burial corrosion or effects in laboratory cultures; little attention has been focused on the importance of these organisms in the marine environment. The natural exposure data from both NRL studies indicate a dominant role for these anaerobic bacteria in the corrosion of structural ferrous metals in the ocean. At all locations, including the half-salinity of Chesapeake Bay, marine sulfate-reducing bacteria were active on the metal. By the end of the first year's exposure, iron sulfide byproducts were found generally over most of the specimen surfaces. Pitting on all panels was moderate, and isolated barnacles and spots of heavy fouling attachment did not seem to induce deeper pitting underneath. Where the anaerobic bacteria were active a soft, nonadherent layer, which seemed to be mostly iron sulfide, formed over all of the metal surfaces beneath the accumulated corrosion and fouling products. With this layer present, the covering material of fouling and corrosion scale can be easily removed in large unbroken pieces. Figure 9 shows a panel with the fouling scale cover partially removed. It appears from

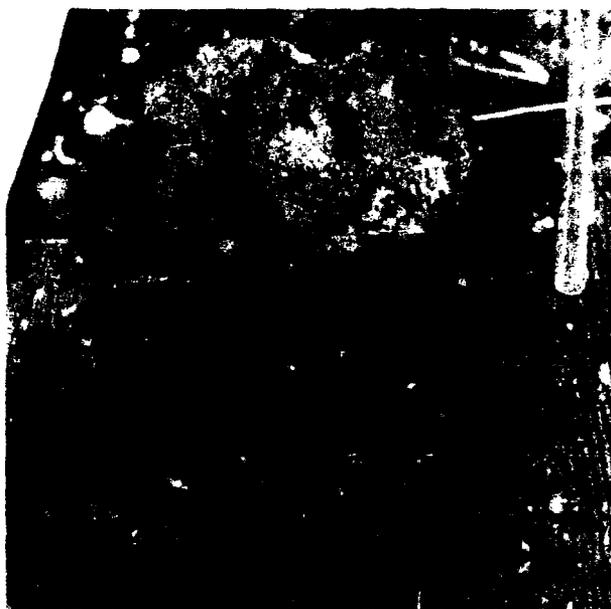


Fig. 9—Steel disk with the outer fouling scale cover laid back to show the soft, black underlying sulfide layer that forms adjacent to the metal surface

these exposures that, at all sites, after a sufficient amount of fouling cover develops, anaerobic conditions are established at the metal surface and the corrosion process becomes bacterially controlled.

The fact that all the different forms of fouling, from algae to a very heavy barnacle cover, barred the passage of oxygen sufficiently to permit the development of sulfate-reducing bacteria at the metal surface, indicates that corrosion rates can be drastically lowered in most seawater environments if the sulfate-reducing bacteria can be selectively inhibited.

BIOLOGICALLY CONTROLLED CORROSION RATES AT DIFFERENT GEOGRAPHICAL LOCATIONS

After the biological processes of marine fouling and marine bacteria have exerted their influences, the corrosion rates are stabilized to a final steady state. Although some of the data from the five NRL sites is very short term, it appears that all final rates will fall within a range of 2-3 mpy. This is considerably lower than the marine corrosion rates for carbon steel usually reported in the literature (>5 mpy); however, such literature reports almost invariably include the initial high first-year loss. This initial corrosion is of no great significance in itself, but if used with short-term results to establish a corrosion rate it can be very misleading. If 3 mpy can be accepted as a reasonably consistent upper limit for most low-velocity seawater environments, design engineers will have considerably more latitude in the use of structural steels in seawater.

To investigate additional geographical locations and to establish steady-state corrosion rates from longer exposures, data have been examined from all known seawater corrosion studies where adequate information was obtained for carbon steel (14-17). Curves from these studies show much the same pattern as those for the NRL sites; after initial high losses, the corrosion rate levels off to a steady state. It can be assumed that these linear relations result from the combined activity of fouling and sulfate-reducing bacteria. The first-year losses and final constant rates for seven different ocean sites were presented in Table 2. The best-fit lines for the linear portion of the time-vs-corrosion curves were used to determine these steady-state corrosion rates. Even though temperatures, bio-fouling, and seasonal growing cycles are quite varied for the seven sites, which range in latitude from 9° N to 51° N, once the corrosion rate has stabilized the final steady-state rates are all within the narrow limits of 2-3 mpy.

Whereas the large differences in water temperature between these extremes of latitude would have considerable effect on normal aqueous corrosion, with bacterial corrosion the temperature effect is less significant; the *Desulfovibrio* bacteria that corrode steel are known to thrive between 10° C and 40° C and to be active over most of this range (18).

All of the exposure results reported in Table 2 are for relatively clean, low-velocity, inshore seawater, suitable for the growth of both macrofouling and marine microorganisms. Polluted or diluted seawater, arctic seawater, high-velocity water, and other waters in which oxygen is present but in which marine fouling cannot thrive could produce higher corrosion rates. Furthermore, these results were obtained with descaled samples that had edge-to-area ratios of 0.056 and no dissimilar metal contacts. Higher edge-to-area ratios could increase the average metal loss. Galvanic effects caused by large areas

Table 2
Corrosion Rates of Carbon Steel in Seawater at Various Locations

Exposure Location	North Latitude (dy)	Duration of Exposure (yr)	First-Year Loss (Av Penetration mpy)	Steady-State Corrosion Rates* (Av Penetration, mpy)
Panama Pacific Naos Is., C.Z.	8.55	16	5.8	2.7
Panama Caribbean Coco Solo, C.Z.	9.21	1.5	3.6	<3.0
Key West, Fla.	24.35	2.0	3.7	<2.9
Kure Beach, N.C.	33.85	8	5.7	2.2
Point Mugu, Calif.	34.06	2.1	5.8	<2.4
Harbor Is., N.C.	34.20	2.5	4.5	<2.1
Emsworth, Eng.	50.80	4	4.0	<2.1

*Slope of the linear portion of the time-corrosion curve (after the first year).

of mill scale, dissimilar metal contact, or variations in electrolyte seem to override bacterial control and accelerate pitting. Other variations from normal conditions could be expected to dominate or influence corrosion rate control.

ESTIMATION OF METAL LOSS FOR EXTENDED PERIODS OF EXPOSURE

From the data in Table 2, 2.0-2.5 mpy seems to be a reasonable range for average penetration in normal temperate-climate seawater, while 2.5 to 3.0 mpy seems to best represent the range in tropical seawater. With these values in hand, equations for estimating the life of structural steel in normal inshore seawaters can be simply derived as follows.

The general equation for average penetration of steel in seawater is

$$\bar{P}_t = \bar{P}_1 + R_c(t - 1), \quad (1)$$

where

\bar{P}_t = average penetration in mils at time t in years

\bar{P}_1 = average penetration in mils for the first year of exposure

R_c = constant corrosion rate in mpy (slope of the linear portion of the time-vs-corrosion curve).

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For temperate seawater (where $R_c < 2.5$ mpy),

$$\bar{P}_t < \bar{P}_1 + 2.5(t - 1). \quad (2)$$

For tropical seawater (where $R_c < 3.0$ mpy),

$$\bar{P}_t < \bar{P}_1 + 3.0(t - 1). \quad (3)$$

Thus for any time t the average corrosion penetration can be estimated if the first-year loss is known or can be approximated. Since in extended projections P_1 is only a minor consideration, an approximate value of 5 mils (based on the results in Table 2) can be used for both tropical and temperate exposures without introducing appreciable error. Equations (2) and (3) can then be reduced to

$$\bar{P}_t < 2.5t + 2.5 \quad \text{for temperate seawater,} \quad (4)$$

and

$$\bar{P}_t < 3.0t + 2.0 \quad \text{for tropical seawater.} \quad (5)$$

These formulas indicate that the estimated average penetration of a carbon steel surface after 10 years of service would be no more than 28 mils for temperate and 32 mils for tropical seawater.

Very little useful corrosion loss information from actual unprotected structures has been reported; such data could be applied to check the validity of these formulas. One report, by Larrabee (19), gives the average penetration of steel H piles exposed in unpolluted seawater near Santa Barbara, Calif. as 40 mils over a 20-yr period. This is in fairly good agreement with the <53 mils predicted by Eq. (4).

SUMMARY

The data obtained from long- and short-term exposures of structural carbon steel in natural aqueous environments have shown the important influence of marine organisms on the corrosion rates of ferrous metals in seawater.

Very high corrosion rates, up to 16 mpy, were measured during initial periods of exposure prior to development of a macrofouling cover.

The length of the prefouling period, the types and quantities of fouling, and the corrosion losses during the first year of exposure varied considerably for the different ocean locations.

By the end of 1 to 1.5 years of exposure, most of the test specimens had become covered with a mat of fouling organisms. These natural covers, although different in composition at the different sites, all seemed to offer considerable protection to the steel panels.

The beneficial effect of the natural protective fouling coating diminishes appreciably when it becomes sufficiently thick (and bio-active) so as to exclude oxygen from the metal surface. Then sulfate-reducing bacteria take control of the corrosion process, and in the anaerobic environment maintained at the metal surface by the self-healing fouling cover, a final steady-state corrosion rate is established. These final rates are surprisingly consistent for the different ocean locations.

In normal temperate and tropical seas, where both fouling organisms and sulfate-reducing bacteria are active, structural steel, after the first year of exposure, generally corrodes at a steady-state rate between 2 and 3 mpy. The rate of 3.0 mpy appears to be the upper limit for corrosion in tropical seawater, while the upper limit found for temperate climate seawater is about 2.5 mpy.

With these low rates established, the design of steel structures to allow for expected loss, in lieu of more costly protective maintenance procedures, becomes a practical consideration.

To utilize fully the natural self-healing protective coatings provided by marine fouling, methods of attracting fouling to a metal surface and of maintaining a healthy coating on the metal would have to be studied.

In conjunction with the fouling investigation, studies of procedures for controlling the anaerobic sulfate-reducing bacteria population should be undertaken; if these bacteria can be selectively controlled while maintaining an adequate fouling cover, then very low corrosion rates for bare steel immersed in seawater should be attainable.

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REFERENCES

1. "Corrosion of Metals in Tropical Environments," a series of five articles in *Corrosion*
 - a. "Part 1 - Five Non-Ferrous Metals and a Structural Steel," B.W. Forgeson, *et al.*, 14, 73t (1958).
 - b. "Part 2 - Atmospheric Corrosion of Ten Structural Steels," C.R. Southwell, *et al.*, 14, 435t (1958).
 - c. "Part 3 - Underwater Corrosion of Ten Structural Steels," B.W. Forgeson, *et al.*, 16, 105t (1960).
 - d. "Part 4 - Wrought Iron," C.R. Southwell, *et al.*, 16, 512t (1960).
 - e. "Part 5 - Stainless Steel," A.L. Alexander, *et al.*, 17, 345t (1961).

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2. "Corrosion of Metals in Tropical Environments," a series of four articles in *Materials Protection*
 - a. "Aluminum and Magnesium," C.R. Southwell, *et al.*, 4(12): 30-35 (1965).
 - b. "Copper and Wrought Copper Alloys," C.W. Hummer, Jr., *et al.*, 7(1) 41-47 (1968).
 - c. "Nickel and Copper-Nickel Alloys," C.R. Southwell and A.L. Alexander, 8(3): 39-44 (1969).
 - d. "Structural Ferrous Metals," C.R. Southwell and A.L. Alexander, 9(1): 14-23 (1970).
3. C.R. Southwell, "The Corrosion Rates of Structural Metals in Sea-Water, Fresh Water and Tropical Atmospheres," *Corrosion Sci.* 9(3): 179-183 (1969).
4. C.R. Southwell and A.L. Alexander, "Marine Corrosion of Cast and Wrought Non-Ferrous Metals," Proc. 25th Conf. NACE (1970).
5. N.I. Ishchenko and I.B. Ulanovskii, "The Protective Effects of Aerobic Bacteria Against Corrosion of Carbon Steel in Seawater," *Mikrobiol.* 32(3): 521-25 (1963).
6. "Bacteria as a Cause of Corrosion," *Corrosion Prev. Contr.* 15(2): 21 (Mar-Apr. 1968).
7. C.A.H. von Wolzogen Kuhr and L.S. van der Vlugt, "The Graphitization of Cast Iron as an Electrochemical Process in Anaerobic Soils," *Water* (The Hague) 18: 147-165 (1934).
8. R.F. Hadley, "The Influence of *Sporovibrio desulfuricans* on the Current and Potential Behavior of Corroding Iron," in "Bureau of Standards Soil Corrosion Conference Proceedings," St. Louis, 1943, p. 76.
9. L.A. Rozenberg, "Role of Bacteria in the Electrochemical Corrosion of Steel in Seawater," *Mikrobiol.* 32(4): 689-94 (1963).
10. G.H. Booth, P.M. Cooper, and D.S. Wakerley, "Corrosion of Mild Steel by Actively Growing Cultures of Sulphate-Reducing Bacteria," *Brit. Corrosion J.* 1: 345 (1966).
11. W.P. Iverson, "Microbiological Corrosion," *Corrosion Prev. Contr.* 16(1): 15-19 (Feb. 1969).
12. J.R. Postgate, "Recent Advances in the Study of the Sulfate-Reducing Bacteria," *Bacteriol. Rev.* 29(4): 425-41 (1965).
13. D.J. Crisp and P.S. Meadows, "The Chemical Basis of Gregariousness in Cirripedes," *Proc. Roy. Soc B*, 156: 500-20 (1962).
14. J.C. Hudson, "Corrosion of Bare Iron or Steel in Sea Water," *J. Iron Steel Inst.* 166: 123-36 (1950).
15. Personal correspondence with M.W. Lightner (1968), Applied Research Laboratory, U.S. Steel Corp.
16. Personal correspondence with T.P. May and D.B. Anderson (1968), Marine Corrosion Laboratory, International Nickel Co.
17. F.M. Reinhart and J.F. Jenkins, "Corrosion of Materials in Surface Seawater After 12 and 18 Months of Exposure," Naval Civil Engineering Laboratory Technical Note N-1213 (Jan. 1972).

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18. J.D.A. Miller and A.K. Tiller, "Microbial Corrosion of Buried and Immersed Metal," in *Microbial Aspects of Metallurgy* (J.D.A. Miller, editor), New York, Elsevier (1970), pp. 61-105.
19. C.P. Larrabee, "New Data Show That Steel Has Low Corrosion Rate During Long Sea Water Exposure," *Mater. Protect.* 1(12): 95 (1962).