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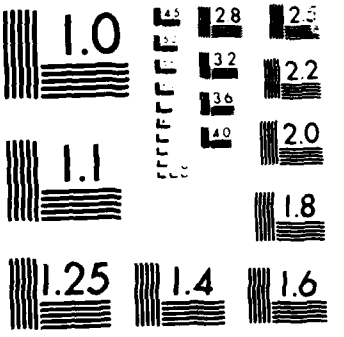

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NRL Memorandum Report 5527

Marine Corrosion

A. J. SEDRIKS

Environmental Effects Branch
Material Science and Technology Division

April 24, 1985

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The report is a review of marine corrosion of metals and alloys which is to be included in the new Handbook of Ocean Engineering, to be published by Academic Press in 1985. The report describes marine environments, the types of marine corrosion encountered, cathodic protection and alloys used in marine applications. Emphasis is placed on describing the types of corrosion generally found and the preventative measures employed. Published key references are noted throughout the text.

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MARINE CORROSION

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1. MARINE ENVIRONMENTS

Marine environments can be conveniently characterized in terms of a number of zones, namely atmospheric, splash, tidal, quiet seawater and bottom-mud zones. These zones provide conditions of varying severity of corrosion, as indicated by the changes in the corrosion rate of carbon steel shown in Figure 1[1].

In the first zone, namely the marine atmosphere, the corrodent is provided by wind-borne salt particles and moisture. The corrosivity of the marine atmosphere therefore varies with wind velocity and direction, height above water, humidity, rainfall, temperature, and factors such as presence of coral dust and pollution. The corrosivity of the marine atmosphere generally decreases with distance from the sea. The amount and frequency of rain is also a factor since it may rinse off salt residues. Corrosion on sheltered sides may be worse since air-borne sea salt particles may not be washed off by rain.

For seagoing vessels marine atmospheric corrosion may be minimized by coating topside structures with an active (e.g. zinc rich) primer coat and an epoxy topcoat to protect the primer. The thickness of the active metal primer coat can also be increased by flame spraying molten metal (e.g. zinc or aluminum) onto the surface to be protected, followed by topcoating with an epoxy paint. Details of the flame spraying procedures are described in References 2 and 3.

Materials residing in the splash zone are wet most of the time. For bare carbon steel this is the most corrosive of the various zones, Figure 1. As in the case of marine atmosphere, corrosion can be minimized by the use of active primer plus epoxy topcoats in the case of steel or by the use of corrosion resistant alloys such as molybdenum-containing stainless steels. For the latter the high degree of aeration in the splashing water promotes the development of passive (i.e. non-corroding) behavior. Biofouling, under which crevice corrosion can occur for stainless steels, generally does not take place in the splash zone.[4]

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In the tidal zone biofouling may occur up to the high-water level. Biofouling may be reduced by the use of anti-fouling coatings[5] or by the use of copper alloys[6] which develop a cuprous oxide corrosion product toxic to marine organisms. Stainless steels containing less than 6% molybdenum in the austenitic grades[1] can exhibit crevice corrosion under natural hard shell fouling. In seawater handling systems biofouling may also be reduced or prevented by chlorination.

The "quiet seawater" zone shown in Figure 1 may give rise to a variation in corrosion and fouling behavior. The shallow waters near the shore are usually saturated with oxygen and often contain sufficient nutrients for biofouling. Protective coatings and/or cathodic protection is generally used for corrosion control. A calcareous scale may deposit on the cathodically protected material, in addition to biofouling. The deep ocean seawater may differ from the surface seawater in terms of oxygen, temperature, pH and salinity, Figure 2[7]. These parameter changes may significantly alter the corrosion behavior of materials such as carbon steel and aluminum alloys. Generally the extent of corrosion and fouling is less in the deep ocean seawater than in surface or near-shore seawater.[4]

The bottom mud zone can also vary in its corrosive characteristics. In terms of chemistry, it can be more corrosive when it contains sulfides. It can also limit access of oxygen to the alloy surface, thereby acting like a crevice.

In considering corrosion resistance in the marine environment, attention should therefore be paid to both the intended service of the structure or component and the specific zone in which the structure or component is to reside during this service. In selecting materials consideration should also be given to the modification of corrosion behavior by the demands imposed by marine technology, such as elevated temperatures, tensile stresses, cyclic stresses, severe (tight) crevices, galvanic coupling and high seawater velocities.

2. TYPES OF MARINE CORROSION

Seawater, with its high dissolved salt content, is an extremely aggressive corrodent for metals and alloys. The mechanism of corrosion in seawater is electrochemical in nature. The theoretical basis for electrochemical corrosion is derived from the mixed potential theory, the formulation of which in its modern form is usually attributed to Wagner and Traud (8). In essence this theory separates the oxidation and reduction reactions of corrosion and postulates that the total rates of all the oxidation reactions equal the total rates of all the reduction reactions on a corroding surface.

Oxidation reactions, referred to as anodic, because they occur at the anodic sites on a corroding metal or at the anode in an electrochemical cell, can be represented by the general reaction

$$M \rightarrow M^{+n} + ne.$$

This is the generalized corrosion reaction that removes the metal atom by oxidizing it to its ion. In this reaction the number of electrons produced equals the valence of the metal ion produced. The mixed potential theory

proposes that all the electrons generated by the anodic reactions are consumed by corresponding reduction reactions. Reduction reactions are known as cathodic, because they occur at the cathodic sites of a corroding metal or at the cathode of an electrochemical cell. The more common cathodic (electron consuming) reactions encountered in aqueous corrosion are as follows:

1. Reduction of hydrogen ions $2H^+ + 2e \rightarrow H_2$.
2. Oxygen reduction (acid solutions) $O_2 + 4H^+ + 4e \rightarrow 2H_2O$.
3. Oxygen reduction (basic or neutral solutons) $O_2 + 2H_2O + 4e \rightarrow 4OH^-$.
4. Metal ion reduction $M^{+n} + e \rightarrow M^{+(n-1)}$.
5. Metal deposition (plating) $M^{+n} + ne \rightarrow M$.

For a metal such as carbon steel corroding in aerated seawater the predominant cathodic reaction is that designated by reaction 3.

Among the predominant modes of corrosive attack in seawater are:

(a) General corosion
(b) Galvanic corrosion
(c) Pitting
(d) Crevice corrosion
(e) Dealloying
(f) Exfoliation corrosion
(g) Erosion corrosion and cavitation
(h) Stray current corrosion
(i) Stress corrosion cracking
(j) Corrosion fatigue

2.1 General Corrosion

The term general corrosion is used to describe attack that proceeds in a relatively uniform manner over the entire surface of the metal. An example is bare carbon steel corroding in natural aerated seawater. The metal or alloy becomes thinner as it corrodes until its thickness is reduced to the point at which failure occurs.

In the case of carbon and low alloy steels exposed in quiet seawater, general corrosion rates do not decrease with time and do not usually vary greatly from steel to steel. This is illustrated in Table 1[9]. It should be noted that when carbon and low alloy steels are used for continuous exposure to seawater, they are cathodically protected. In the case of ship hulls, steels are painted with a corrosion resistant paint and an anti-fouling paint and are then cathodically protected.

2.2 Galvanic Corrosion

When two different metals are immersed in seawater, each will establish its own corrosion potential, E_{corr}. If the values of E_{corr} are significantly different for the two metals, and they are in contact or electrically connected, the metal with the more noble E_{corr} will become predominantly cathodic and the metal with the more active E_{corr} will become predominantly anodic. A measurable current will flow between the anode and the cathode. The corrosion rate of the anode will be increased and the corrosion rate of

the cathode decreased or entirely stopped. The increased corrosion of the anodic material produced by coupling to a cathodic material is known as galvanic corrosion. Galvanic effects can be very important in marine hardware systems using many different alloys. In designing multimetal systems for marine service it is extremely important to select the more noble alloys for the key or critical components.

A simple practical assessment of whether two different metals are likely to produce galvanic corrosion in seawater can be obtained by measuring and comparing the E_{corr} values. If the E_{corr} values differ by hundreds of millivolts, clearly galvanic corrosion is very likely to occur, whereas if the difference is of the order of tens of millivolts galvanic corrosion is less likely. However, sometimes the welding of two alloys even with small differences in E_{corr} values can lead to increased corrosion of the more active material. It is therefore good practice to test welded specimens of dissimilar metals in sea water to determine whether galvanic corrosion is likely to be a problem.

In an attempt to provide an indication of which metal or alloy combinations are likely to cause galvanic corrosion in seawater, a chart of E_{corr} values of various metals and alloys in seawater has been developed, Figure 3[10]. Galvanic coupling of materials exhibiting noble E_{corr} values with materials exhibiting active E_{corr} values is likely to lead to galvanic corrosion of the active material.

In considering galvanic attack on the less noble member, a very important factor is the ratio of the areas of the anodic and cathodic materials. An unfavorable area ratio is one which comprises a large cathode and a small anode. Since for a given current flow in a galvanic cell the current density is greater on a small electrode than on a larger one, a small anode will have a greater current density and hence a greater corrosion rate than a large anode. Hence, in multimetal marine hardware systems best results are obtained when the key or critical components are cathodic and comprise a small area, and the less-critical components, which may be anodic, comprise a large area. Tabulations exist[11] of materials which are galvanically compatible in fastener applications and in pump and valve trim applications in seawater.

2.3 Pitting

Pitting, as the name suggests is a form of localized corrosive attack that produces pits. A metal or alloy that depends on an oxide film for corrosion resistance will pit when conditions are such that the protective film breaks down at local areas by chemical attack. Pitting can be a destructive form of corrosion in engineering structures if it causes perforation of equipment or creates stress raisers in critical areas. However, shallow surface pitting that does not cause perforation is sometimes tolerated and accepted for economic reasons. Aluminum alloys are particularly prone to pitting in seawater. Stainless steels, however, rarely develop pits on the open surface in seawater, and when pitting is seen it is usually associated with deposits or fouling which have produced crevices and is known as crevice corrosion[1].

Commercially produced alloys contain numerous inclusions, second phases and regions of compositional heterogeneity, and there has been a growing body of literature reporting results that identify the initiation of pitting with structural heterogeneities at the surface, particularly, but not exclusively, with inclusions[12].

The propagation of pits is thought to involve the dissolution of metal and the maintenance of a high degree of acidity at the bottom of the pit by the hydrolysis of the dissolved metal ions. There is a relatively wide acceptance of this propagation mechanism, although all its facets are not fully understood. The anodic metal dissolution reaction at the bottom of the pit, $M \rightarrow M^+ + e$, is balanced by the cathodic reaction on the adjacent surface, $O_2 + 2H_2O + 4e \rightarrow 4OH^-$. The increased concentration of M^+ within the pit results in the migration of chloride ions (Cl^-) to maintain neutrality. The metal chloride formed, M^+Cl^-, is hydrolyzed by water to the hydroxide and free acid,

$$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^-.$$

The generation of this acid drops the pH values at the bottom of the pit to low values while the pH of the bulk solution remains neutral.

As in the case of general corrosion, pitting can be prevented by cathodic protection.

2.4 Crevice Corrosion

Like pitting, crevice corrosion also occurs on metals and alloys that depend on an oxide film for protection, such as stainless steels and aluminum alloys. Crevice corrosion is a form of localized corrosion that can occur within crevices or at shielded surfaces where a stagnant solution is present. Such crevices can be formed at metal/metal or metal/non-metal junctions, such as those associated with rivets, bolts, gaskets, valve seats, or surface deposits. In ambient-temperature sea water crevice corrosion can also occur under fouling, particularly under hard-shell fouling.

The mechanism of crevice corrosion in chloride solutions is relatively well understood in terms of a sequence of events involving oxygen depletion, chloride-ion concentration, metal-ion build up, local acidification by the hydrolysis of metal ions, the breakdown of the protective film, and lateral coalescence of attacked sites[10].

Table 2 gives a summary of the types of crevices in which problems have been either frequent or infrequent. Problems are usually encountered in tight crevices. However, tightness is difficult to quantify since the width of a tight crevice is determined by asperity contact and the extent of deformation, or in some cases fracture, of the touching asperities. Thus, under certain circumstances it is the surface finish, often not a well defined parameter, which may determine the critical variable of crevice geometry.

The initiation of crevice corrosion can be minimized or prevented by cathodic protection or the selection and use of more highly alloyed materials (sometimes used as weld overlays).

Regarding velocity, it has been shown[13] that keeping water flowing at a high velocity will prevent crevice corrosion by preventing fouling. The practicability of using velocity to prevent crevice corrosion may be questionable, however, since if flow is interrupted enabling growths to attach, restoring flow will not remove them[10].

Regarding cathodic protection, zinc, aluminum, or carbon steel anodes are suitable for prevention of crevice corrosion of Type 316 stainless steel[14].

Among alloys that are reported to be resistant to crevice corrosion in seawater in tight metal-to-non-metal crevices are titanium alloys[4], the high molybdenum nickel base alloys Hastelloy alloy C-276 and Inconel alloy 625[1], and the high chromium superferritic stainless steels[15]. Austenitic stainless steels containing about 6% molybdenum are reported to be resistant to crevice corrosion in seawater in the less severe crevices formed by natural hard-shell fouling[1].

2.5 Dealloying

Dealloying, parting or selective leaching are the terms used to describe a form of corrosion in which one alloying element (usually the more electrochemically active one) is preferentially removed from the alloy. The remaining material is porous and weak. In seawater this form of corrosion is known to occur in high zinc brasses in which zinc is removed leaving behind spongy red copper. For brasses this corrosion process is known as dezincification.

Two theories have been proposed to explain dezincification. One proposes that the zinc is selectively leached from the brass leaving a porous residue of metallic copper in situ, while the other proposes that both copper and zinc are dissolved and that the copper immediately re-deposits back onto the surface of the metal.

Dezincification can occur uniformly over the surface as a layer or in the form of rounded areas known as "plugs". The plug-type of attack propagates in depth leading to perforation.

Dezincification can occur over a wide range of pH, although pH appears to affect the form of the attack. The layer type of dezincification is favored when the environment is acidic and the brass has a high zinc content. The plug type of dezincification is more prevalent when the environment is neutral or slightly alkaline and the zinc content is relatively low. In both cases dezincification is favored by stagnant conditions, by the presence of chloride ions and by the formation of deposits that lead to stagnant solution conditions. The attack is more severe in crevices.

Dezincification of alpha brass can be prevented by alloying with arsenic, antimony and phosphorus at levels of 0.02 to 0.06% of these elements[16]. No alloying elements have been found that prevent the dezincification of the higher zinc alpha-beta brasses and the use of these materials should be avoided in environments which cause dezincification.

Dealloying is also known to occur, although less frequently, in copper-aluminum alloys (i.e. dealuminification) and copper-nickel alloys (denickelification) in acid environments[4,16].

2.6 Exfoliation Corrosion

Certain sheet or plate aluminum alloys, such as the 5000 series and the 7000-series, in certain heat treatment conditions (i.e. tempers), tend to corrode preferentially along planes parallel to the rolling plane. This form of attack is called exfoliation corrosion. The corroded plate consists of alternating strata of corroded and uncorroded metal.

Exfoliation corrosion has been known to occur in alloy 5456 in the H343 temper, in alloy 5086 in the H34 temper, and in alloys 7039, 7075, 7079 and 7178 in the T6 temper. In these alloys exfoliation corrosion is intergranular and related to heat treatments that precipitate corrodable intermetallic particles along the alloy grain boundaries which are aligned in the direction of rolling.

In Al-Zn-Mg-Mn alloys (e.g. 7004) exfoliation corosion can be transgranular[17]. Under severe service conditions such as those involving moisture and chlorides, it is necessary to protect Al-Zn-Mg-Mn alloys. Products in the hot rolled state will be susceptible to exfoliation and consequently may need overall protection. Both spray metallizing and metal cladding with an anodic alloy have been shown to be very effective in offering such protection.

2.7 Erosion-Corrosion and Cavitation

Erosion-corrosion or impingement attack can be defined as the acceleration of attack caused by a rapidly flowing corrodent sometimes containing solid particles capable of causing erosion or wear. Protective films, and even the metal surface itself, are removed by the abrasive action of a fluid at high velocity. In general, the higher the velocity the more abrasive the solution.

Since a corrosion effect is superimposed on a mechanical erosion process, resistance to this form of attack is determined by a balance of properties that enhance resistance to corrosion and ones which enhance resistance to erosion (e.g., hardness of the alloy).

Accelerating factors are turbulence (turbulent flow causes greater erosion-corrosion than lamellar flow) and designs that cause impingement (e.g., sharp elbows in piping where the fluid is forced to change its direction of flow). Obvious remedies include the use of more resistant alloys, changes in design, cathodic protection, and removal of suspended solids. Weld overlays of corrosion-resistant materials can provide a practical solution in cases where the other remedial measures are not desirable.

Typical velocities that are encountered in marine technology are 40 ± 5 ms^{-1} for hydrofoils, 25 ms^{-1} (max) at the periphery of pump impellers, and 5 ms^{-1} (max) in piping systems. Erosion-corrosion is a problem with copper alloy shipboard piping and the limiting design velocities as a function of alloy and pipe diameter are shown in Table 3[18]. The molybdenum-containing

austenitic stainless steels are considered to have a high resistance to erosion-corrosion[1]. It has been suggested[1] that there is a threshold velocity for austenitic stainless steels in flowing uncontaminated seawater, of the order of 50 ms^{-1}, although the introduction of large amounts of hydrogen sulfide and acidification, which can occur as a result of the decay of animal organisms, will bring this threshold velocity for Type 316 stainless steel down to about 25 ms^{-1}.

Cavitation damage is a form of attack that occurs under conditions in which the relative velocity between the liquid and the solid material is very high. In technology it is encountered in pumps, ships propellers, and hydraulic turbines under certain combinations of design and operating conditions and a fundamental understanding of the phenomenon requires knowledge of hydro-mechanics. In essence, a liquid experiencing flow divergence, rotation, or vibration forms low-pressure areas that generate cavities or bubbles. These cavities form and collapse with extreme rapidity, generating intense shock waves. The collapse of the cavities on a solid surface removes material by mechanical erosion. The observation that cavitation damage can occur on glass and plastics rules out the view that the phenomenon is basically a corrosion process. However, corrosion can accelerate cavitation damage of metals and alloys in corrosive environments, and sometimes cause attack under mild cavitating conditions which by themselves only rupture protective surface films.

Alloys such as Inconel alloy 625, Hastelloy alloy C-276, and the molybdenum-containing austenitic stainless steels, are considered to have a high resistance to cavitation damage[11]. Thus, if cavitation damage is localized, repair weld overlays with Inconel alloy 625 may prove useful. However, for severe cavitating conditions redesigning the components to improve the flow characteristics of the liquid may be necessary, since upgrading to more corrosion-resistant materials may be of limited use.

2.8 Stray-Current Corrosion

Stray-current corrosion is caused by the flow of direct current from a source through seawater to a ship hull or other metallic structure in the seawater. Direct current will corrode most metals in a conductive solution and the severity of the corrosion will depend on the quantity of the current discharged. With most structural alloys stray-current corrosion will occur at the location where the current is discharged from the corroding structure into the water. However, in the case of aluminum and zinc corrosion may also occur at the location where the stray currents are picked up from the water, because of the formation of excessively alkaline conditions at such locations. Aluminum alloys are particularly prone to stray current corrosion.

Stray-current corrosion is generally more severe on coated structures than on bare structures because the discharged current will be concentrated at and will flow from defects or damaged areas in the coating.

The sources of stray currents are generally difficult to locate. Stray current can be provided by improperly grounded welding power sources, industrial equipment and electrical railway tracks which employ direct current for operation.

2.9 Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a general term describing alloy failures that occur by the propagation of cracks in corrosive environments. The requirements for SCC to occur are the presence of tensile stresses such as may be provided by service loads, welding, fit-up or heat treatment and a corrodent such as seawater. The cracks form and propagate roughly at right angles to the direction of the tensile stress at stress levels much lower than those required to fracture the alloy in the absence of the corrodent. When stress corrosion cracks have progressed to a depth at which the remaining load bearing section of an alloy reaches its fracture stress in air, the material separates by normal overload fracture. Failures, when they occur, therefore tend to be catastrophic and hence receive much attention.

Among alloys known to exhibit SCC in seawater are high strength steels, high strength titanium alloys in the presence of notches or fatigue cracks, high tensile alpha-beta brass and manganese propeller bronze, high strength aluminum alloys in the short transverse direction, and high strength martensitic and precipitation hardened stainless steels. For detailed listings of various alloys susceptible to stress corrosion cracking in marine environments the reader should consult Reference 19.

Stress corrosion failures in the high strength alloys are often facilitated by the entry of hydrogen into the metal and are accordingly often referred to as hydrogen embrittlement failures. The hydrogen can be produced by certain cathodic corrosion reactions described earlier or by cathodic protection procedures implemented to minimize corrosion. The use of high strength alloys in seawater under conditions of cathodic protection constitutes an intrinsic stress corrosion risk. New designs incorporating tensile stresses should be carefully analyzed and evaluated by stress corrosion testing[20] before being put into service.

For high strength alloys a stress corrosion cracking resistance index, K_{Iscc}, has been defined[19] as the stress intensity below which stress corrosion cracking is not expected to occur. For seawater the relevant value of K_{Iscc} should be determined under conditions of cathodic protection if the latter is to be used. An attractive feature of this index is that it enables the specification of the combination of stress and the size of a pre-existing flaw than can be tolerated in a structure without the occurrance of stress corrosion cracking.

If cyclic stresses are anticipated in service, this index may not be relevant and crack growth rates should be determined in the presence of the estimated cyclic stresses in a corrosion fatigue evaluation.

2.10 Corrosion Fatigue

Fatigue is the term used to describe the cracking of a metal under repeated cyclic stresses. Generally fatigue cracks initiate and propagate at stresses below the yield strength after numerous cyclic applications of stress. As in the case of stress corrosion cracking, the fatigue crack propagates until the load bearing section of a material is reduced to the point at which the ultimate tensile strength is exceeded. At that point the material will separate by overload fracture.

The term corrosion fatigue is used to describe fatigue cracking in the presence of environments that may or may not be particularly corrosive to the unstressed material. In most engineering alloys the presence of corrosion seriously degrades the fatigue strength, especially at long fatigue lifetimes (e.g. $> 10^6$ cycles). A convenient way of describing the effect of environment is by comparing the variation of fatigue fracture stress with the number of stress cycles applied (S-N curves) in air and in the environment of interest. It has been the practice in alloy evaluations to compare the corrosion fatigue resistance of various alloys in terms of the stress at which no failure occurs after 10^7 or 10^8 cycles. This stress is often referred to as the corrosion fatigue strength (CFS) after a specified number of cycles (e.g., CFS at 10^8 cycles). CFS should not be equated with or identified as the corrosion fatigue limit. It is not certain whether in some alloy/environment systems there is corrosion fatigue limit.

A listing of CFS at 10^8 cycles for a large number of alloys in seawater, derived from smooth specimens not containing notches, is given in Reference 18. It should be emphasized that laboratory test data of the type described in Reference 18 should not be used directly to predict the service life of components, such as ships propellers. Both the time of exposure of the component to the corrodent and the magnitude and frequency of the stress cycles may be significantly different for a component in service, and these factors should be taken into consideration. Also, cathodic protection can affect CFS and this should be taken into account. Corrosion fatigue strength (e.g. CFS at 10^8 cycles) in seawater can be reduced by the presence of notches and surface defects which act as stress raisers. Such notches can be produced by welding defects, pitting, crevice corrosion or stress corrosion cracking. Thus, for many engineering applications consideration of corrosion fatigue must incorporate the presence of pre-existing cracks. For this reason engineers often study the rate at which corrosion fatigue cracks grow[21] in order to be able to predict the remaining life of cracked structural components. Examples of simplified engineering procedures for summing the remaining fatigue life in cracked components, including the effects of corrosion, are given in References 22 and 23.

3. CATHODIC PROTECTION

Cathodic protection employing sacrificial anodes is in essence the practical utilization of galvanic corrosion to protect one component of the galvanic couple. As shown in Figure 3, the coupling of low alloy steel ($E_{CORR} \approx -0.6$ volts vs S.C.E.) to zinc (($E_{CORR} \approx -1.0$ volts vs S.C.E.) will produce a couple in which the steel will become the cathode (non-corroding member) and zinc will become the sacrificial anode (rapidly corroding member). The couple will only function effectively if the anode is in good electrical contact with the cathode (i.e. the ohmic resistance of the electrical path is less than about 0.01 ohm) and there is a good electrolytic path between the anode and the cathode through the seawater. For a detailed practical account of cathodic protection the reader should consult Reference 24.

Of the metals showing very active corrosion potentials in seawater (Figure 3) zinc, aluminum and magnesium can serve as sacrificial anodes. None of these are used as the pure metals, but in the form of dilute alloys

in which the alloying elements prevent the formation of passive films which would otherwise render the sacrificial anodes ineffective. A popular anode for ships has been zinc produced under the anode grade specification MIL-A-18001G of the U. S. Navy.

Regarding aluminum alloy sacrificial anodes, there are many commercially produced grades with varying alloy chemistry. These are generally known by trade names such as Galvalum I, Galvalum III, Deltalum III, Aloline BA778 and others. A continuing problem with aluminum anodes is in the area of end-user quality control, since the performance of some anodes may depend not only on composition but also on heat treatment. Moreover, some aluminum anodes contain mercury as an alloying addition which is an undesirable element from the environmental point of view.

The disadvantage with magnesium anodes, is that although they are thermodynamically effective, they may corrode too quickly to give an economic anode life in seawater.[25]

Regarding current densities required for protection, experience has shown that a current density of about 5 to 10 mA/ft^2 is sufficient to protect bare steel in seawater. According to producers of zinc anodes, one standard zinc anode measuring 12x3x1.25 inches and weighing 12 lbs. can deliver about 350 ampere hours/pound. Thus, a single anode of this size would protect about 100 square feet of bare steel for about 14 months. Painting of the steel cathode greatly reduces the required cathodic protection current. The exact reduction of current by painting may depend on the type of paint used and method and care of application.

Cathodic protection is a specialized subject and it is recommended that the designers of large, complex and critical structures for seawater use call upon cathodic protection specialists to design the cathodic protection corrosion control system. The direct electric current provided by the sacrificial anode can be replaced by a direct current source or a rectified and controlled alternating current source. Impressed current cathodic protection is used in instances where the attachment and replacement of sacrificial anodes is not desirable. For details regarding impressed current protection systems the reader should consult Reference 24.

4. ALLOYS FOR MARINE ENVIRONMENTS

4.1 Steels

Steels are the most widely used materials of construction for marine applications. They are used for hull structures, penetration fittings, superstructures, buoys, cables and other applications. Because of their poor corrosion resistance in seawater they require cathodic protection. Among low strength steels that have seen extensive use for marine applications are AISI grades 1020, 1040, 1080, 1095 and HY-80. The higher strength grades such as AISI 4340, HY-100, HY140, and HY-180 are also used. However, as the strength level is increased the steels may begin to exhibit susceptibility to hydrogen embrittlement, particularly in the presence of cathodic protection, notches, weldments, or hydrogen sulfide in the seawater. Some guidelines for steel selection in terms of hydrogen embrittlement resistance are provided in References 26 and 27.

4.2 Stainless Steels and Nickel-Base Alloys

Most low-molybdenum stainless steels exhibit crevice corrosion in seawater and hence require cathodic protection for satisfactory use. The higher molybdenum grades and molybdenum-containing nickel base alloys have also been used in critical applications in marine technology[1], as shown in Table 4. In addition to the alloys shown in Table 4, the duplex stainless steel Ferralium alloy 255 and the superferritic stainless steels 29-4C and SEA-CURE have been used for marine hardware and seawater cooled condenser tubing, respectively, because of their resistance to crevice corrosion. The nickel base alloy, Monel alloy 400, is used for sheathing pilings and other marine structures[28] in the splash zone.

4.3 Copper Alloys

Copper alloys are widely used in marine technology for piping, valves, fittings, propellers, tanks, hardware, bellows, and electric wiring. Several hundred different copper alloys have been developed and are listed in Reference 29. The main alloy categories are brasses, bronzes, and cupronickels. In recent years cupronickels have become popular materials for marine applications. For a description of the copper alloys used for marine applications the reader should consult Reference 30. Among the specific problems experienced with copper alloys in seawater are dealloying and erosion-corrosion, as described earlier. Only brasses inhibited by alloying against dezincification should be used in seawater[31].

4.4 Aluminum Alloys

Among the many aluminum alloys available commercially, the following have seen most use in marine service: 6061, 5052, and 5056. For all aluminum alloys corrosion protection is desirable in seawater by the use of coatings or cathodic protection. In the unprotected state aluminum alloys may exhibit pitting, crevice corrosion and exfoliation corrosion. Also, because aluminum alloys exhibit active corrosion potentials, Figure 3, they are prone to galvanic corrosion when coupled to more noble metals. For the behavior of specific aluminum alloys in marine environments the reader should consult Reference 30.

4.5 Titanium Alloys

For seawater, unalloyed titanium is one of the most corrosion resistant structural materials available. The yield strength of unalloyed titanium ranges from 40 ksi to 90 ksi. Higher strength titanium alloys, such as Ti-6%Al-4%V (yield strength = 120 ksi (min)) are also available. Unalloyed titanium and Ti-6%Al-4%V also exhibit high resistance to stress corrosion cracking and corrosion fatigue. Higher strength titanium alloys such as Ti-8%Al-1%Mo-1%V exhibit stress corrosion cracking when tested in thick sections in the presence of a notch.[32]

The limited use of titanium and its alloys in seawater applications is basically a matter of cost.

5. TRADEMARKS

The use of trademarks or other proprietary alloy designations in the text has been necessary for purposes of exact description and is common practice. In no case does identification by trademarks imply recommendation or endorsement by any parties associated with this publication, nor does it imply that any material so identified is either the only material available or necessarily the best for any given application. The ownership of trademarks used in the narrative is as follows:

Trademark	Producer
Cor-Ten	United States Steel Corporation
Inconel	Inco family of companies
Incoloy	Inco family of companies
AL6X	Allegheny Ludlum Steel Corp.
254 SMO	Avesta Jernverks AB
IN 862	Inco family of companies
UHB 904L	Uddeholms Aktiebolag
2RK65	Sandvikens Jernverks AB
20Cb3	Carpenter Technology Corp.
29-4C	Allegheny Ludlum Steel Corp.
Sea-Cure	Colt Industries
Ferralium	Bonar Langley Alloys, Ltd.
Monel	Inco family of companies
Galvalum	Dow Chemical
Deltalum	Delta Corrosion, Inc.
Aloline	British Aluminum Company
Hastelloy	Cabot Corporation

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Table 1

Long-Term Corrosion Rates for Steels Exposed to Quiet Seawater

Material	Exposure Duration, years	Corrosion Rate, mm/yr.
AISI 1020	15	0.05
COR-TEN	15	0.11
AISI 4340	7	0.13
HY-80	7	0.11

Table 2

Experience with Crevice Corrosion in Service Equipment

Frequent Problems	Infrequent Problems
Metal-to-metal crevices	
Bolt head to washer	Sleeve to pump shaft
Washer to base plate	Tube to tube sheet
Bolt thread to nut thread	
Wire rope	
Root pass of pipe welds with incomplete fusion	
Attachment pads to vessel wall	
Fillet-welded rib to deck	
Metal-to-non-metal crevices	
O-ring to polished surface	Valve-stem packing
Gasket to flange face	Pump-shaft packing
Telfon to metal	Dirt deposits
Polyethylene tape to metal	Rubber gasket to metal in plate-type heat exchangers
Barnacle to metal	Sand or mud deposits
Silicone to metal	
Molybdenum disulfide to metal	
Graphite-lubricated gasket to metal	

Table 3

Limiting Design Velocities for Copper Alloys in Seawater Piping Systems

Alloy	Limiting Design Velocity (ft/sec) Pipe Sizes		
	Under 3 in.	4 to 10 in.	Over 10 in.
Copper and silicon bronze	2	3	3
Red brass	3	4	4
Aluminum brass	6	8	10
90-10 Cupronickel	8	10	12
70-30 Cupronickel	10	12	15

Conversion factors:
1 in = 25.4 mm
1 ft/sec = 0.3048 ms^{-1}

Table 4

Some Documented Marine-Related Applications of Fe-Cr-Ni-Mo Alloys

Alloy	Applications
Inconel Alloy 625	Weld overlays for shafts and seals, exhaust-system expansion joints, patrol-boat propellers, submarine auxiliary propulsion motors, submarine quick-disconnect fittings, submarine transducer controls, steam-line bellows, undersea cable sheathing, oceanographic instruments, flare booms and tips, rudder actuators
AL 6X Stainless Steel	Sea water-cooled power-plant condensers
254SMO Stainless Steel	Sea water-cooled power-plant condensers, seawater coolers for chemical plants, plate heat exchangers, offshore gas compressors, ballast tank pipes for tankers
IN 862 (cast)	Multistage pumps for re-injection of sour waters
UHB 904L, 2RK65, 20Cb3 Stainless Steels	Seawater coolers of chemical and petrochemical plants
Inconel Alloy 718	Hydrofoil components and vapor compression rotors in desalination plants
Incoloy Alloy 825	Offshore platform equipment for gas handling, shipboard scrubbers, marine exhaust systems, expansion bellows
Type 316 Stainless Steel	Linings in desalination plant flash chambers and cathodically-protected cast pump components
CN7M (cast) Stainless Steel	Pumps

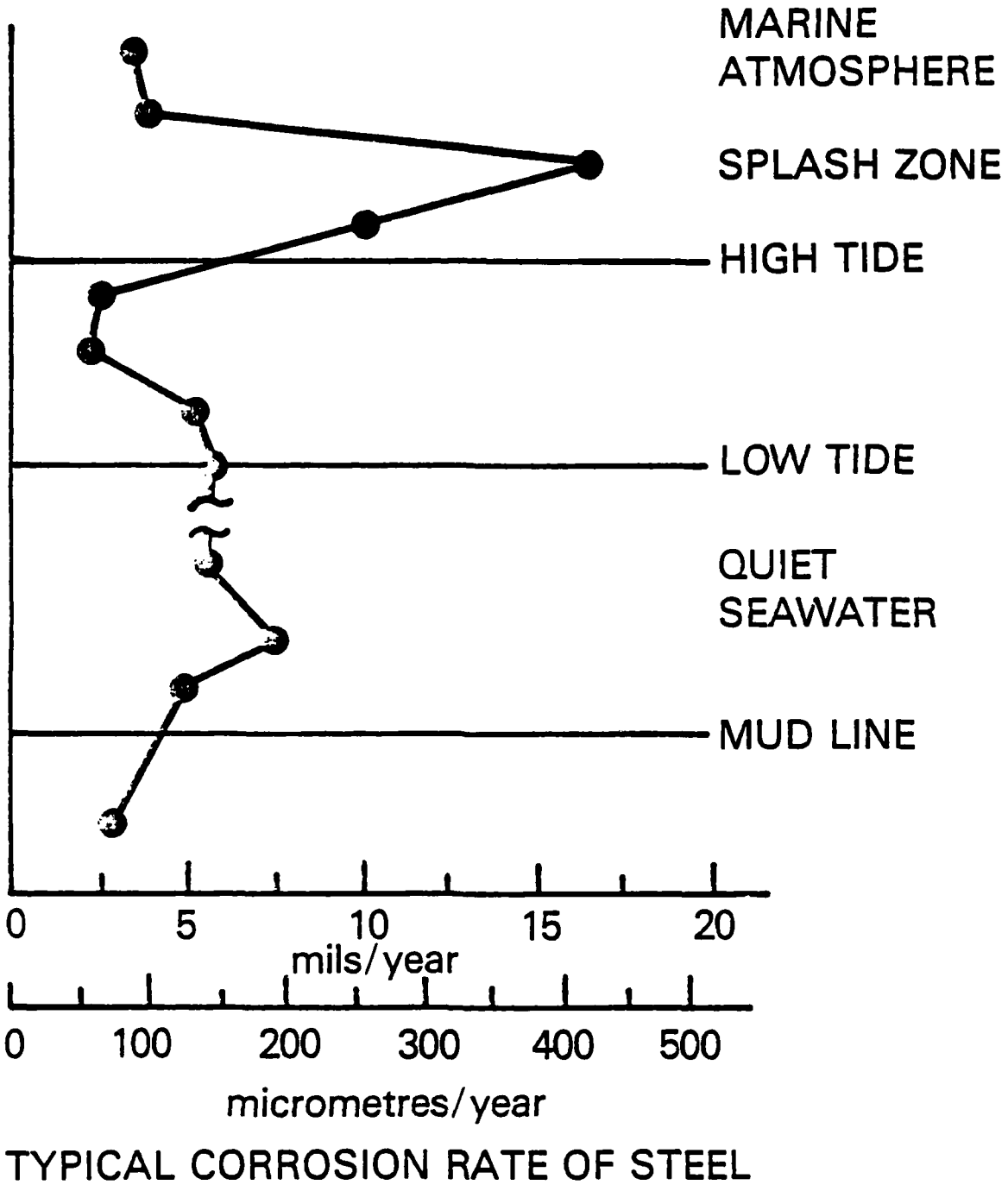

Fig. 1 — Typical corrosion rates of steel in various marine environments

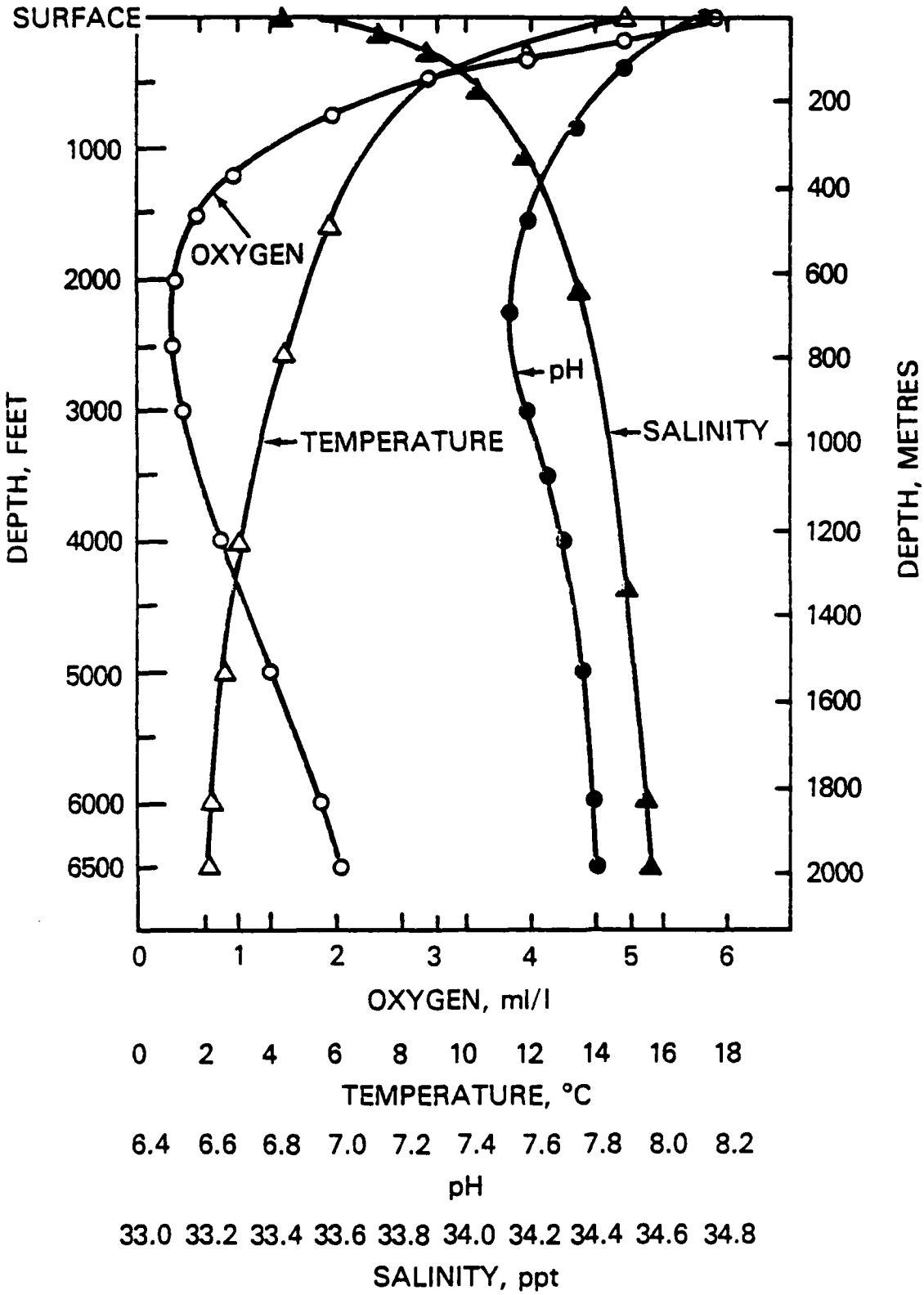

Fig. 2 — Variations in seawater with depth at a pacific ocean test site

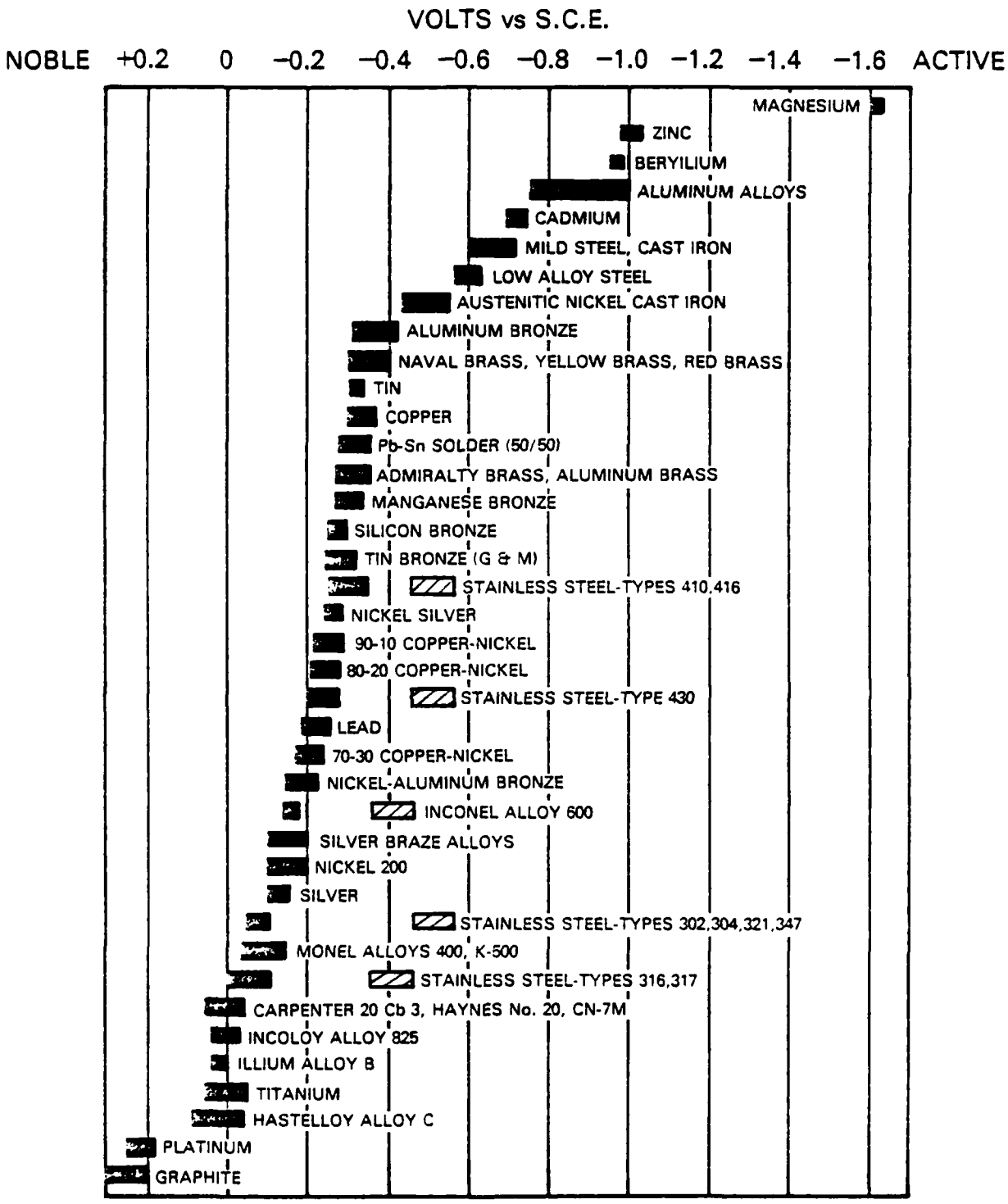

Fig. 3 — Corrosion potentials of various materials in flowing seawater (2.5 to 4 m/s) at temperatures in the range 10°C — 26°C. The hatched symbols indicate potentials exhibited by stainless steels in acidic water such as exists in crevices.

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