Manual of 2

INDUSTRIAL CORROSION STANDARDS AND CONTROL

F.H.Cocks

STP 534

'الالال' AMERICAN SOCIETY FOR TESTING AND MATERIALS

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MANUAL OF INDUSTRIAL CORROSION STANDARDS AND CONTROL

Sponsored by ASTM Committee G-1 on Corrosion of Metals

ASTM SPECIAL TECHNICAL PUBLICATION 534 F. H. Cocks, editor

List price \$16.75 04-534000-27



AMERICAN SOCIETY FOR TESTING AND MATERIALS 1916 Race Street, Philadelphia, Pa. 19103

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> Printed in Baltimore, Md. November 1973

Foreword

The Manual of Industrial Corrosion Standards and Control has been prepared and sponsored by the members of ASTM Committee G-1 on Corrosion of Metals. Dr. Franklin H. Cocks was responsible for the organization of this material.

Related ASTM Publications

Metal Corrosion in the Atmosphere, STP 435 (1968), \$27.00 (04-435000-27)

Localized Corrosion—Cause of Metal Failure, STP 516 (1972), \$22.50 (04-516000-27)

Stress Corrosion Cracking of Metals—A State of the Art, STP 518 (1972), \$11.75 (04-518000-27)

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Frontispiece: Photograph of U.S. 35 Highway Bridge, Point Pleasant, W.Va. taken after its collapse on 15 Dec. 1967. Courtesy National Transportation Safety Board.



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Introduction

This manual is a working source book of procedures, equipment, and standards currently being used to solve industrial testing and control problems. It is intended as a guide to those in university and government, as well as in industrial laboratories, who are faced with combatting corrosion problems or developing more corrosion resistant materials. The aim throughout is to combine a brief discussion of fundamental principles with clear descriptions of concomitant techniques and methods as well as the types of problems to which these have been and are being applied.

Although corrosion problems are common to all industries, the test methods and control procedures that have been developed to deal with them are diverse. By combining descriptions of major corrosion problem areas together with discussions of the approaches that have been evolved for controlling them, more effective means for reducing corrosion losses may be fostered. Thus, this manual is organized so that the first chapter provides a concise introduction to basic corrosion science, while subsequent chapters, each written by a leader in his field, review the application of these principles in practice. Emphasis is placed on the explanation of proven methods and standards, as well as on suggestions for procedures which might well become standards in the future. These chapters are followed by two appendices. The first provides abstracts and sources for existing corrosion standards, while the second appendix includes six ASTM standards referred to most frequently in the text.

Within the past decade it has become clear to an increasing number of diverse scientific and industrial groups that more emphasis on the standardization of corrosion tests and the means for interpreting data derived from them is both necessary and valuable. It is often difficult, however, when faced with a specific corrosion problem, to know which of several different testing procedures and standards should be utilized or where information directly relevant to a particular situation might be obtained. It is hoped that this manual will assist in resolving this difficulty.

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Chapter 1

Introduction to Corrosion

F. H. $Cocks^1$

Webster $[1]^2$ defines corrosion as "the action or process of corrosive chemical change . . . a gradual wearing away or alteration by a chemical or electrochemical essentially oxidizing process as in the atmospheric rusting of iron." This definition does not restrict corrosion to any one class of materials, nor to any one environment. It does, however, imply a degradation in properties through the reaction of a material with its surroundings. This environment may be liquid, gaseous, or even solid as in the case of the reaction of filaments of SiC with an aluminum matrix they are intended to reinforce. Although many such new corrosion reactions are being encountered as more complex materials are applied in increasingly varied and unusual situations, the problems associated with far more mundane and widespread corrosion reactions have by no means been satisfactorily solved. The formation of oxides on iron exposed to the atmosphere at both ambient and elevated temperatures, for example, in automobile mufflers, year after year continues to extract a cost of hundreds of millions of dollars. Considerable progress has been and continues to be made, however, in reducing these corrosion losses. It is to the further control and reduction of practical and industrially important corrosion problems that this manual is directed.

Corrosion studies and the development of improved methods of corrosion prevention and control are of enormous practical industrial importance. It has been estimated that in the United States alone, the costs attributable to corrosion amount to more than 10 billion dollars annually [2]. While some corrosion losses may appear inevitable, the proper selection of materials and the application of known principles and protection methods can be expected to reduce these losses greatly.

In this introductory chapter, the basic principles of corrosion science are reviewed as a guide to subsequent chapters which each provide a discussion of how this knowledge can be applied in industrial practice to achieve the desired goal—the minimization of the economic burden imposed by corrosion. The unifying theme throughout these chapters is the use of

² Italic numbers in brackets refer to references listed at the end of this chapter.

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standards which accurately detail the testing methods and control procedures now carried out in major industries. It is to be hoped that the information provided will contribute not only to the more effective and widespread use of available standards but to the development of additional corrosion standard test methods and control procedures as well.

The attack on metals by their environment can take many forms, ranging from uniform general attack and tarnishing to more complex reactions such as pitting, filiform corrosion, corrosion fatigue, stress corrosion, and other specific forms of damage discussed later in this chapter. The type of property degradation that will occur depends not only on the nature of the metallic material, and its physical state and conditions of use, but on the composition of the environment as well. The specific chemical species present in this environment, their concentration, and the temperature can determine whether attack will be general or localized or whether it will be fast or slow, accelerated or inhibited. The physical structure of many metals of a given composition can be enormously altered by heat treatment or cold working, and this structure in many cases will determine whether attack will be catastrophic or relatively mild.

In evaluating and correcting an existing or potential corrosion situation there are several fundamental choices to be considered. Does the metal or alloy being considered represent an optimum choice both from the point of view of economics as well as corrosion resistance? What will the environmental conditions this alloy is exposed to be and is it feasible to consider modifying this environment? What limits are imposed on the design of the structure being considered and how can this design be changed to minimize corrosive effects? Can protective coatings be used to isolate the whole structure, or critical parts of it, from the environment? The design engineer, too, can influence corrosion processes, not only directly through the specification of materials but also by providing material and environment configurations that minimize corrosive effects. Such designs can only be optimized if the processes that might lead to damage are understood.

While the range of possible corrosion situations is so large that a description of even a small fraction of them is not practical, a surprisingly few basic principles are sufficient to understand the detailed mechanisms of each case. Once the mechanism of damage is understood, the likelihood of making the correct choice to eliminate or minimize this damage is greatly improved.

In the following section, these underlying principles of corrosion processes are described before going on to consider important special forms of corrosion attack and methods of corrosion protection and control.

Basic Corrosion Principles

The conversion of elemental metals or alloys into ions in an electrolyte (any electrically conducting solution, for example, seawater) is an essentially electrochemical process. The electrochemical character of corrosion has long been firmly established, and a concise review of the early experimental proofs of the electrochemical basis of corrosive action is available [3]. When a metal is placed in an electrolyte it acquires an electrical potential which is a measure of the tendency for that metal to dissolve as positive ions in solution. Since the solution must remain electrically neutral, an equivalent number of some other positive ions must be removed as the metal corrodes. A sample of iron placed into a solution of copper sulfate, for example, will begin to corrode (dissolve as iron ions) while at the same time copper ions are plated out of solution forming copper metal on the surface of the iron. The dissolution of the iron can be written as

$$Fe \rightarrow Fe^{++} + 2e^{-}$$
 (1)

and is said to be an anodic reaction because the solid iron (Fe) is being increased in oxidation state to form iron ions (Fe⁺⁺), by the removal of two electrons $(2e^{-})$ per iron atom. The copper reaction can be written as

$$Cu^{++} + 2e^{-} \to Cu \tag{2}$$

and is said to be a cathodic reaction because copper ions are being reduced in oxidation state through the gain of electrons, to form copper metal. The combination of reactions 1 and 2 gives

$$Fe + Cu^{++} \rightarrow Fe^{++} + Cu$$
 (3)

as the overall electrochemical reaction. This corrosion reaction is selfstifling, however, because the deposited copper acts as a barrier between



FIG. 1-Schematic drawing showing the corrosion of zinc in dilute hydrochloric acid.

the iron and the solution, thus preventing further reaction. In the case of zinc immersed into acid solutions, it is hydrogen which is plated out from solution in order to maintain electrical neutrality, as shown in Fig. 1. Here, the electrons released by the zinc as it ionizes and goes into solution travel through the remaining solid zinc to the points on the surface where hydrogen ions are neutralized to form hydrogen atoms. Two such neutralized atoms must then combine to form a molecule of hydrogen gas. Since the hydrogen gas can be removed as bubbles, the reaction is not a self-limiting one, and the formation of zinc chloride is not stifled.

In both corrosion reactions just described, the flow of electrons occurs within the specimen of corroding metal itself. This current flow could just as well pass through an external wire to neutralize ions at some other point, as for example, at a piece of copper immersed elsewhere in the solution as shown in Fig. 2. In such a case, the corroding sample (zinc) is defined as the anode and the copper sample, which does not corrode, as the cathode.

The tendency for zinc to enter the solution is dependent upon the concen-



FIG. 2—Schematic drawing showing the separation of anodic and cathodic relations when strips of zinc and copper in hydrochloric acid are electrically connected.



FIG. 3-Schematic drawing of a metal-ion concentration corrosion cell.

tration of zinc ions already present in this solution. For example, one could construct a corrosion cell as shown in Fig. 3, by placing two zinc specimens in solutions containing different concentrations of zinc ions. In this case the zinc sample which is immersed in the less concentrated zinc solution will corrode while the zinc specimen immersed in the more concentrated zinc solution will have additional zinc plated on it. This process is an example of concentration cell corrosion and illustrates the point that corrosion can occur even if the metals making up the anode and the cathode are identical.

The electrical potential reached by a metal immersed in an aqueous solution thus depends on the concentration of its ions already present in solution. The electromotive force series shown in Table 1 lists the potentials acquired by different metals when each is in contact with an aqueous solution of its ions at unit activity (approximately 1 mole/1000 g of water at 25 C) [4]. The zero potential assigned to hydrogen is selected arbitrarily and thus constitutes the reference potential against which the others have been measured. Very reactive metals such as sodium and magnesium appear at the negative or less noble end of the list, while inert metals such as platinum or gold appear at the more noble or positive end.

Reaction	Standard Electrode Potential, volts
$\begin{array}{l} Au^{+++} + 3e^- = Au \\ Ag^+ + 1e^- = Ag \\ Cu^{++} + 2e^- = Cu \\ 2H^+ + 2e^- = H_2 \\ Pb^{++} + 2e^- = Pb \\ Sn^{++} + 2e^- = Pb \\ Sn^{++} + 2e^- = Ni \\ Cd^{++} + 2e^- = Ni \\ Cd^{++} + 2e^- = Cc \\ Fe^{++} + 2e^- = Fe \\ Cr^{+++} + 3e^- = Cr \\ Zn^{++} + 2e^- = Zn \\ Al^{+++} + 3e^- = Al \\ Mg^{++} + 2e^- = Mg \end{array}$	+1.50 Noble (more cathodic) +0.7991 +0.337 0.00 -0.126 -0.136 -0.250 -0.40 -0.440 -0.74 -0.763 -1.66 -2.37 Active (more anodic)

TABLE 1—Standard electromotive force series (emf) at 25 C [4].

As an example of how such a scale can be used, one can imagine a corrosion cell constructed as shown in Fig. 4. Here one compartment contains a specimen of zinc in a solution of zinc ions at unit activity (approximately 1 mole of zinc ions per 1000 g of water). The other compartment contains a specimen of silver in a solution of silver ions also at unit activity. A voltmeter connected between these two metal specimens would read 1.562 V as would be expected from their relative position in Table 1. Then, when the voltmeter is replaced by a copper wire, the more active zinc will be found to corrode, while the less active silver is plated from solution. As this process continues, the voltage measured between the zinc and silver specimens would decrease as the concentration of zinc ions increased while that of silver ions decreased. Thus, corrosion cell potentials depend on both the electrode material and the electrolyte composition.

In addition to the standard emf series of Table 1 it is also useful to know cell potentials obtained using a single common electrolyte. Such a listing is called a galvanic series and the relative position shown by a group of metals and alloys immersed in seawater as the standard electrolyte is shown in Table 2. If a pair of metals selected from this list are immersed in seawater and connected together electrically, the metal lower on the list will be found to corrode. The farther apart the metals of this pair are, the greater will be the tendency for the lowermost one to corrode. It must be remembered that this list applies only to a specific electrolyte—seawater—and a much different sequence could result if some electrolyte other than seawater were chosen.

As illustrated for the case of zinc in hydrochloric acid, corrosion reactions can be divided into two parts. In the case of zinc in hydrochloric acid, the anodic (corrosion) reaction is that involving zinc entering solution.

Anodic Reaction:
$$Zn \rightarrow Zn^{++} + 2e^{-}$$
 (4)



FIG. 4-Schematic drawing showing the voltage developed between two standard half cells.

The second part is the cathodic reaction of the hydrogen required for electrical neutrality of the solution.

Cathodic Reaction:
$$2H^+ + 2e^- \rightarrow H_2$$
 (5)

There are not many practical situations, however, in which metals are used in sufficiently acid solutions that hydrogen gas evolution occurs. In many service environments corrosion is decreased by the formation of a thin film of hydrogen gas on the cathodic surfaces which decreases the current flow and hence the corrosion rate. This situation is known as hydrogen polarization. If this film of hydrogen is destroyed or prevented from forming, the corrosion rate will be increased. The presence of dissolved oxygen can lessen hydrogen polarization by shifting the potential to more active values and reacting with the hydrogen to form water.

$$O_2 + 2H_2 \text{ (or } 4H) \rightarrow 2H_2O \tag{6}$$

Noble (more cathodic)	Platinum Gold Graphite Silver Chromium Nickel Stainless Steel Type 304 (passive) Chromium Nickel Stainless Steel Type 316 (passive) 13% Chromium Steel Type 410 (passive) Titanium Monel 70-30 Cupro-Nickel Silver Solder Nickel (passive) 76Ni-16Cr-7Fe Alloy (passive) Yellow Brass Admiralty Brass Aluminum Brass Red Brass Copper Silicon Bronze Nickel (Active) 76Ni-16Cr-7Fe Alloy (active) Muntz Metal Maganese Bronze Naval Brass Lead Tin Solders Lead Tin Chromium Nickel Stainless Steel Type 304 (active) Chromium Nickel Stainless Steel Type 316 (active) Chromium Stainless Steel Type 410 (active) Mild Steel Wrought Iron Cast Iron Aluminum (2024) Cadmium Aluminum (6053) Alclad Zinc Magnesium Alloys
Active (more anodic)	

TABLE 2—Galvanic series of metals and alloys.

It is also possible for dissolved oxygen to participate directly in the cathodic reaction by being reduced to hydroxyl ions.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{7}$$

In either case the presence of dissolved oxygen acts to depolarize the cathodic reaction and leads to an increased rate of corrosion by increasing the rate at which metal ions can enter the solution.

During corrosion, more than one oxidation process and more than one reduction process may occur simultaneously. This situation would be expected, for example, if the corroding metal were an alloy containing two or more elements or if the solution environment contained more than one reducible species. If, for example, the dilute acid in Fig. 1 also contained dissolved oxygen, then both oxygen reduction as well as hydrogen reduction could occur, leading to a higher corrosion rate for the zinc in oxygencontaining acid than in deaerated acid. The anodic reaction, on the other hand, would be increased if species were present which could form complexes with the metal's ions, thus lowering the effective concentration of such ions in solution. Conversely, inhibitors can act to slow the rate of corrosion by interfering with the cathodic reaction, the anodic reaction, or both, as discussed in Methods of Corrosion Prevention and Control of this chapter.

In many practical corrosion situations in natural environments under nearly neutral or alkaline pH conditions, the rate of corrosion is substantially determined by the concentration of oxygen. As was shown in Fig. 3, corrosion can occur between two identical metals if the concentration of their ions in solution varies. Similarly, a corrosion cell will also be formed if the concentration of dissolved oxygen varies, as illustrated in Fig. 5. In this figure, the sample on the right is the cathode while the sample on the left corrodes and is the anode, because of the difference in oxygen concentration and the resultant ease with which the cathodic reaction (Eq 7) can occur. There are many practical situations where such a difference in oxygen concentration can arise, as for example in the case of crevice corrosion discussed in the next section where the oxygen deficient conditions inside the crevice favor the anodic corrosion reaction. Oxygen concentration cell corrosion is indeed a widespread form of attack. In a tank that is only partially full of water, for example, the water at the top will contain more oxygen than the rest, and the metal touching this oxygenated water will be cathodic to the remainder of the tank. Similarly, scale, rust, or other surface deposits can lead to oxygen concentration cell corrosion by limiting the oxygen supply to specific local areas.

In addition to these effects, the relative area of metal on which the anodic and cathodic reactions occur is also important in determining corrosion rates. If, for example, the area in solution of the specimen of iron labeled B in Fig. 5 were doubled relative to that of specimen A, the corrosion rate of specimen A would be increased. This increase would occur because the greater area available for the cathodic reaction (Eq 7) would increase the rate at which this oxygen reduction reaction could occur. Conversely, the rate of corrosion would be reduced if the area of specimen B were decreased.

Effects such as this can be readily understood with reference to an Evans diagram [5] as shown in Fig. 6. In this diagram, the changes in potential which occur for both the anodic and cathodic reactions are shown as a function of the current which flows between the anode and the cathode. As may be seen, the potentials of each reaction approach each other as the current increases. That is, each reaction becomes polarized as its rate



FIG. 5-Schematic drawing of an oxygen concentration corrosion cell.

increases. In the case of the oxygen reduction reaction, this polarization becomes particularly severe at relatively low currents because of the low solubility of oxygen in solution. That is, at relatively low currents it begins to require substantial changes in potential to produce slight increases in cathodic current because the available dissolved oxygen at the cathode is depleted (diffusion control). The corrosion rate, which is proportional to the current flowing $(i_1, i_2, \text{ or } i_3)$ is fixed by the intersection of the anodic and cathodic curves. As shown in the figure, increasing the area of the cathode (or increasing the oxygen concentration) will increase the overall corrosion rate by decreasing the degree of polarization of the cathodic reaction. Similarly, the overall amount of corrosion would also be increased if the area of the anode were increased although this increase would be relatively small if, as shown, oxygen diffusion to the cathode were the limiting factor.

In the case just described, the corrosion reaction is said to be under cathodic control since the greatest change in potential occurs in the cathodic reduction reaction. In still other cases, the corrosion rate may be limited by the electrical resistance of the electrolyte. In this latter case, the potentials at which the anodic and cathodic reactions occur are not equal but differ by the voltage drop which occurs through the electrolyte. Evans diagrams



FIG. 6—An Evans diagram illustrating the effect of increasing anodic or cathodic area on corrosion where oxygen diffusion is the limiting factor.

illustrating these three situations are shown in Fig. 7. Such diagrams are useful in interpreting many different corrosion effects and extended discussions of such uses are available [6,7,8].

The extremely important phenomenon of passivity can also be understood by considering the way in which the rate of the anodic (corrosion) reaction of certain metals varies with potential or, alternatively, with the oxidizing power of the corrodent (corrosion solution).

Table 1, for example, shows that zinc is electrochemically much less active than aluminum. Yet Table 2 shows that aluminum is cathodic to zinc in seawater. This corrosion resistance of aluminum is due to the presence of an adherent film of oxide on its surface. For metals such as stainless steel this film may be extremely thin but will still give protection in oxidizing environments. In reducing environments, however, this oxide film is removed and the steel becomes active. The corrosion resistance of titanium alloys depends similarly on the presence of protective, passive films. There are, in fact, two distinct types of passive behavior. In the case of lead in sulfuric acid, for example, a passive protective film is formed in dilute solutions and the corrosion rate remains very low, until in more concentrated acid solution, the film becomes increasingly soluble and the corrosion rate increases. For the case of iron in nitric acid solution, however, a different passive behavior is observed. In dilute nitric acid, iron



FIG. 7—Evans diagrams showing corrosion reactions which are under (a) cathodic control, (b) anodic control, and (c) solution resistance control.

corrodes at a high rate. As the concentration of acid is increased this corrosion rate at first increases, as shown in Fig. 8. At a critical HNO₃ concentration, however, a further increase in acid concentration causes a very large drop in corrosion rate, due to the formation of a protective, passive film on the iron. If the acid concentration is reduced to the initial dilute condition the corrosion rate will remain low, because the passive film is retained. However, this passive film is then unstable, and the original high corrosion rate can be restored by scratching or tapping the iron sample.



FIG. 8—Evans diagram showing the corrosion behavior of iron in dilute and in concentrated nitric acid, illustrating the onset of passivity.

Passivity may thus be broadly defined as the decrease in corrosion susceptibility exhibited by certain metals and alloys brought about by the generation of protective films or adsorbed layers in particular environments where they would be expected to corrode readily. The importance of this phenomenon in determining the corrosion behavior of many imporant alloy systems, such as stainless steel and titanium alloys, cannot be overemphasized and has lead to a large number of investigations. Concise reviews of this work and current theories on the nature of passive film alloys are available [9, 10].

The corrosion of iron, like that of all other metals, is strongly dependent not only on potential but also on the pH of its solution environment. From available thermodynamic and electrochemical data it is possible to construct a diagram which shows the regions of potential and pH where certain species are stable. These diagrams are usually referred to as Pourbaix diagrams in honor of the man who first suggested their use. In using them, it is to be emphasized that no rate information can be obtained and only equilibrium data are involved. Figure 9 shows, for example, a simplified Pourbaix diagram for iron in water [11]. In this diagram the only solid substances considered are Fe, Fe_3O_4 and Fe_2O_3 . A slightly different diagram



FIG. 9—Simplified Pourbaix (potential-pH) diagram for Fe in H_2O , considering only Fe, Fe₃O₄, and Fe₂O₃ as solid phases.

would be obtained if Fe, $Fe(OH)_2$ and $Fe(OH)_3$ were considered. The potentials given are those which would be measured against a standard hydrogen electrode.

In this diagram, when any reaction involves species other than OH⁻ or H⁺, such as Fe⁺⁺, a concentration of 10^{-6} moles/l is assumed. Thus, the horizontal line dividing the Fe and Fe++ fields indicates that for potentials more negative than -0.62 V, iron will not corrode to form a solution containing more than 10^{-6} moles/l of Fe⁺⁺ ions. Thus, iron is immune to corrosion over the range of potentials and pH values where Fe is the stable species. Conversely, iron will corrode in the range of potentials and pH values where Fe⁺⁺, Fe⁺⁺⁺, or HFeO₂⁻ are the stable species. No information is provided, however, on the rate of corrosion. In those regions where solid Fe_3O_4 and Fe_2O_3 are formed, passive films can be formed, which may give some protection against corrosion. It must also be remembered that the diagram shown in Fig. 9 is for pure iron in water. A different diagram would be needed if either an iron alloy or a solution containing a salt, such as NaCl, were being considered. As data involving practical alloys and common environments become available, Pourbaix diagrams can be expected to come into ever increasing use.

In this section we have shown how differences in both metal and solution composition can give rise to the electrochemical potential differences required to produce corrosion. In the next section we now go on to consider some of the important special forms which this corrosive action can take.

Forms of Corrosion Attack

The previous section has outlined the basic electrochemical principles which underlie corrosion processes. In this section we will describe some of the important specific forms which these corrosion processes can take in aqueous, atmospheric, and soil environments, including a discussion of bacteriological influences and high temperature oxidation processes. This will lead, in the last section, to an outline of the basic approaches which can be used to minimize or prevent corrosion losses.

Uniform Attack

Corrosion which occurs uniformly over the surface of a material is the most common form of damage. It may proceed at a nearly constant rate if the reaction products are soluble or the attack may be self-stifling if these products do not dissolve readily in the corrodent, as we have already seen for the case of iron immersed in a copper sulfate solution. Similarly, in corrosion of silver by a solution of iodine in chloroform, attack slowly ceases as a film of insoluble silver iodide is built up. On the other hand, the attack of unstressed Zn in dilute sulfuric acid also occurs over the entire exposed surface of the zinc. Since in this case the reaction product, zinc sulfate, is soluble, the rate of reaction of the zinc will be constant provided the sulfuric acid is present in excess. In other cases such as the rusting of iron, the build-up of an oxide layer does not prevent further attack because the porous form of the corrosion product does not exclude the environment. Certain special grades of weathering steels now coming into use, however, contain small amounts of alloying elements which lead to the formation of protective oxides that stifle continuing attack. A typical composition for such a steel would be (in weight percent) 0.12C-0.3Mn-0.1P-0.5Si-0.5Cu-1.0Cr-0.5Ni-balance Fe. The way in which these elements influence the corrosion process is still uncertain. It appears, however, to be related to the combined influence of these alloying additions in providing a dense, adherent oxide layer near the metal-oxide interface.

Most commonly, uniform attack occurs on metal surfaces which are homogeneous in chemical composition or which have homogeneous microstructures. The access of the corrosive environment to the metal surface must also usually be unrestricted. As we have seen, corrosion requires both anodic and cathodic areas and on a specimen that is corroding uniformly such areas may be visualized as fluctuating over the surface.

The rate of uniform attack can be evaluated in a straightforward manner, using either weight loss or specimen thickness change measurements. It is important to remember, however, that the rate of attack may vary with time and so measurements should be made at more than one interval. An extreme example of this is shown by the weathering steels mentioned previously where the rates of attack may be initially quite high but continuously decrease as the time of exposure increases. In the case of uniform attack this rate can be expressed as milligrams per square decimeter per day (mdd), inches per year (ipy), or other convenient units. Uniform corrosion attack is quite common, but so too are other forms of corrosion which can make the correct evaluation of corrosion damage more difficult.

Pitting Corrosion

One of the most troublesome forms of corrosion is the formation of pits on metal surfaces. In pitting corrosion, attack is highly localized to specific areas which develop into pits. Active metals such as Cr and Al, as well as alloys which depend on Cr- or Al-rich passive oxide films for resistance to corrosion are prone to this form of attack. Thus, stainless steels and aluminum alloys are particularly susceptible, especially in chloride containing environments. These pits usually show well-defined boundaries at the surface, but pit growth can often change direction as penetration progresses. When solid corrosion products are produced the actual corrosion cavity may be obscured but the phenomenon can still be recognized from the well-defined nature of the corrosion product accumulations. Pitting corrosion is usually the result of localized, autocatalytic corrosion cell action. Thus, the corrosion conditions produced within the pit tend to accelerate the corrosion process. As an example of how such autocatalysis works, consider the pitting attack of aluminum in an oxygenated solution of sodium chloride. Imagine that there exists a weak spot in the oxide film covering the aluminum surface so that the corrosion process initiates at this point. The local accumulation of Al^{+++} ions will lead to a local increase in acidity due to the hydrolysis of these ions. That is, the hydrolysis of aluminum ions gives as the overall anodic reaction:

$$Al + 3H_2O \rightarrow 3H^+ + Al(OH)_3 + 3e^-$$

If the cathodic oxygen reduction reaction, which produces alkali, occurs at a region removed from this anodic reaction the localized corrosion of the aluminum will produce an accumulation of acid. This acid destroys the protective oxide film and produces an increase in the rate of attack. In addition, the accumulation of a positive charge in solution will cause the migration of Cl^- ions to achieve solution neutrality. This increased Cl^- concentration can then further increase the rate of attack. This process is illustrated schematically in Fig. 10. Since the oxygen concentration within the pit is low, the cathodic oxygen-reduction reaction occurs at the mouth of the pit, thus limiting its lateral growth.

Pitting attack can also be initiated by metallurgical inhomogeneities. Magnesium alloys, for example, are very sensitive to the presence of iron particles sometimes imbedded in the surface during rolling. In chloride environments, these iron particles give rise to pits which have pinnacles in their centers, the iron particles resting on the topmost points of the pinnacles. In this case, each iron particle provides a preferred site for the cathodic oxygen reduction reaction and the pinnacle is associated with the outward spread of alkali formed by this reaction.

In most cases pits tend to be randomly distributed and of varying depth and size. The evaluation of pitting damage is difficult and weight loss measurements usually give no indication of the true extent of damage. Measurements of average pit depth can also be misleading because it is the deepest pit which causes failure. Maximum pit depth information is therefore the most useful in estimating equipment service life.

Crevice Corrosion

This form of localized attack occurs when crevices or other partially shielded areas are exposed to corrosive environments. Attack usually arises because of differences in the concentration either of ions or of dissolved gas (for example, oxygen). As we have seen, this difference in solution composition can result in differences in electrical potential even though the metal may be of uniform composition throughout. In general, the region deep within the crevice corrodes while the cathodic reaction takes place at the mouth of the crevice, which is not attacked. As in the case of pitting corrosion, crevice corrosion may be autocatalytic because the hydrolysis of the metal ions being formed within the crevice can lead to high



FIG. 10—Schematic drawing illustrating the autocatalytic nature of pitting attack on aluminum in oxygenated sodium chloride solution.

acidic conditions. The accumulation of positive charge in the solution within the crevice will also lead to an increased concentration of anions and, especially in the case of chloride-containing solutions, this accumulation can lead to more aggressive corrosion conditions. Because of this increased aggressiveness, severe corrosion can often occur at creviced areas even though surrounding, smooth, uncreviced areas remain relatively unattacked.

In the case of metals such as stainless steel, which are normally protected by passive films, crevice corrosion conditions can be particularly dangerous. This is true because the conditions of oxygen depletion existing within the crevice can result in the removal of the protective oxide film. As seen in Table 2, a sample of stainless steel without its protective film is chemically more reactive than one still covered by such a film. A corrosion cell will then be set up between the active region of the crevice interior and the still passive regions outside. It should be noted that crevice corrosion conditions can be brought about if the metal is partially covered or shielded with either nonmetallic material or foreign matter and it is not necessary for the crevice to be entirely metallic. For example, an elastic band placed around a specimen of stainless steel in seawater will initiate severe corrosive attack in the crevice formed between the rubber and the steel.

Galvanic Corrosion

As we have seen, an electrical potential difference will usually exist between two dissimilar metals exposed to a corrosive solution. When these two metals are electrically connected the more active metal will become the anode in the resulting corrosion cell, and its corrosion rate will be increased. The extent of this increase in corrosion rate will depend upon several factors. A high resistance in the electrical connection between the dissimilar metals, for example, will tend to decrease the rate of attack. On the other hand if a large area of the more noble metal is connected to a smaller specimen of the more active metal, attack of the more active metal will be greatly accelerated. This acceleration occurs because, as discussed for the case shown in Fig. 5, the larger cathodic surface will not polarize readily. If oxygen reduction, for example, is the cathodic reaction, a large area of the more noble metal will enable this cathodic reaction to proceed easily. A classic example of this situation would be the use of steel rivets to hold copper plates together. The large area of the more noble (cathodic) copper would lead to the rapid corrosion of the more active (anodic) steel. The reverse situation, the use of copper rivets in steel plates, is not as damaging because the corrosion is dispersed over the relatively large anodic (steel) area, and only a small cathodic (copper) surface is available. Hence the rate of corrosion of the steel will be under cathodic control, and the situation will be that illustrated in Fig. 7a.

The conductivity of the corrosive medium will also affect both the rate and the distribution of galvanic attack. In solutions of high conductivity the corrosion of the more active alloy will be dispersed over a relatively large area. In solutions having a low conductivity, on the other hand, most of the galvanic attack will occur near the point of electrical contact between the dissimilar metals. This latter situation is usually the case, for example, under atmospheric corrosion conditions.

Not all galvanic corrosion is detrimental. Zinc coatings are used to protect steel not because the zinc is resistant to corrosion, but because the zinc corrodes preferentially and hence cathodically protects the steel by making any exposed areas of steel into local cathodes. Magnesium and zinc, which are anodic to steel, when electrically connected to buried steel pipe make this pipe the cathode in the resulting corrosion circuit. Only the sacrificial magnesium or zinc anode undergoes corrosion. A further discussion of cathodic protection as a means of controlling corrosion damage is given in Methods of Corrosion Prevention and Control of this chapter.

Selective Leaching

As its name implies, selective leaching involves the preferential corrosion and removal of one or more electrochemically active elements from an alloy, with the less reactive elements remaining behind. The most common example of this form of attack is dezincification or the selective removal of zinc from brass. This dezincification can be either uniform or localized (plug type). In either case, what remains is a porous residue of essentially pure copper having little or no mechanical strength. Susceptibility to dezincification tends to decrease with decreasing zinc content, and brasses containing less than about 15 weight percent zinc (for example, red brass) are substantially immune. Improved resistance to dezincification can also be achieved through alloying, principally with tin ($\sim 1\%$), arsenic, phosphorus, or antimony ($\sim 0.04\%$), which inhibit the selective leaching process.

Other alloys are also susceptible to selective leaching. Buried grey cast iron piping, for example, can sometimes become "graphitized" through the selective corrosion of iron, leaving behind a porous mass of graphite particles. Since graphite is very cathodic relative to iron, a galvanic corrosion cell is established. As in the case of dezincification, the remaining graphite sponge possesses almost no strength, even though the pipe may appear to be relatively unattacked and its dimensions substantially unchanged. Graphitization does not occur in nodular cast iron since the graphite particles are discrete and do not remain as a porous residue. White cast iron, which has effectively no free carbon, is also immune.

Potentially, any alloy which consists of elements widely separated in electrochemical activity may be susceptible to selective leaching. The silver in gold-silver alloys, for example, can be removed almost completely by corrosion in dilute nitric acid leaving behind essentially pure gold.

Intergranular Corrosion

In many corrosive media, grain boundaries are anodic to grain interiors. In most situations, the reactivity of such boundaries is not great enough, however, to lead to significantly increased damage. The term intergranular corrosion is therefore usually reserved for those particular cases where corrosive attack shows a high degree of localization at grain boundaries in preference to grain interiors, leading to a substantial degradation in mechanical or other properties. This type of attack can occur, for example, in improperly heat-treated stainless steels which do not contain special stabilizing alloying additions. The corrosion resistance of stainless steels depends to a great degree on their chromium content. When non-stabilized stainless steels are heated to between 900 and 1500 F, the precipitation of chromium carbides can occur. Grain boundaries are preferred nucleation

sites for the precipitation of these carbides, and their preferential formation at these boundaries therefore locally depletes the chromium content of the steel. Since the grain interiors still regain a high chromium content, they remain protected. The chromium-depleted zones at the grain boundaries will thus be small anodic areas electrically connected to large cathodic areas, and severe intergranular attack will occur. It is important to note that sensitizing heat-treatment of stainless steel, which produces damaging grain boundary precipitates, can also occur during welding. In this case there will be an area near the weld where the temperature conditions of the welding operation cause grain boundary precipitation of chromium carbides. This precipitation will lead during exposure to corrosive environments to the formation of localized bands of severe intergranular attack (weld decay). Such zones can be avoided if the material is reheat treated after welding to redissolve the carbide precipitates, thus restoring the chromium to the alloy. To combat this problem of intergranular corrosion, stainless steels have been developed which either contain very little carbon or which contain small additions of elements such as columbium and titanium which are strong carbide formers. In either case the effective carbide content of the steel is lowered. The lack of available carbon prevents the formation of



FIG. 11—An electronmicrograph showing precipitate free zones along a grain boundary margin of a sample of Al-4 wt % Cu aged 20 h at 200 C.



FIG. 12—An electronmicrograph showing selective corrosive attack along three grain boundaries in a sample of Al-4 wt% Cu aged 20 h at 200 C and exposed to aerated NaCl solution.

grain boundary chromium precipitates and hence prevents preferred grainboundary attack.

Grain boundary precipitates can also lead to intergranular attack in other alloys besides stainless steels. In Al-Cu alloys, the CuAl₂ precipitate particles can be formed preferentially at grain boundaries, along with concomitant precipitate free zones along the margins of these boundaries, as shown in Fig. 11. These CuAl₂ precipitates are strongly cathodic relative to pure aluminum. Hence, the preferential formation of these precipitates at grain boundaries can lead to selective corrosive attack as shown in Fig. 12. In the case of Al-Zn-Mg alloys, similar preferred precipitation at grain boundaries can also occur, as shown in Fig. 13. In this case, however, the MgZn₂ precipitates are strongly anodic relative to aluminum and are selectively attacked as shown in Fig. 14. In both of these cases involving aluminum alloys, intergranular corrosion is not as severe as in the case of sensitized stainless steels. However, when tensile stress is combined with this selective attack, it is possible for greatly increased damage to result from stress corrosion, as discussed next.



FIG. 13—An electronmicrograph showing the preferred formation of $MgZn_2$ precipitates along a grain boundary in a specimen of Al-7.5 wt % Zn-2.4 wt % Mg alloy aged 72 h at 100 C.

Stress Corrosion

When the combination of tensile stress and corrosion acting together produces greater damage than either applied separately, stress corrosion is said to occur. It is important to note that the tensile stress can either be residual or externally applied. This form of corrosion damage is particularly dangerous because failure can be catastrophic and occur without warning. In general, stress corrosion is highly localized and occurs in the form of cracks. Particularly in the case of high strength aluminum alloys exposed to chloride-containing environments, these stress-corrosion cracks proceed preferentially along grain boundaries. In other cases, however, such as austenitic stainless steels in chloride-containing environments, cracking occurs transgranularly. In still other cases, particularly copper base alloys, cracking can occur either transgranularly or intergranularly depending on the environment.

Susceptibility to stress corrosion is generally measured by the time required to produce fracture after a stressed specimen is exposed to the corrosive environment, and higher tensile stresses produce failure in shorter times than lower tensile stresses. For most susceptible alloys there is usually a lower stress level below which failure does not occur. Other tests have



FIG. 14—An electronmicrograph showing the selective attack of $MgZn_2$ precipitates in a sample of Al-7.5 wt% Zn-2 wt% Mg aged 89 h at 100 C and exposed to an aerated NaCl solution.

been devised to separate the effects of stress and corrosion in materials which are susceptible to stress corrosion [12]. These tests have proved useful in evaluating the effectiveness of such surface treatments as shotpeening, which are used to increase resistance to stress corrosion [13]. In alloys which crack intergranularly for example, it can be shown that a substantial part of the protective effect of shot-peening arises because of surface grain boundary disruption, as well as from residual stress effects.

Whether cracking is intergranular or transgranular, cracks tend to grow in the plane normal to that of the residual or applied tensile stress. In this plane, the stress concentration at the head of the growing crack will be highest and crack growth will be fastest. The resistance of high strength materials to such crack propagation and the influence of corrosive environments on this resistance, can be evaluated by means of precracked specimens [14]. By increasing the load on a specimen of suitable dimensions containing a crack of known size, the stress intensity factor which causes the crack to become unstable and extend can be determined. This factor then gives the fracture toughness of the material under the environmental conditions of the test. Thus, stress corrosion processes clearly involve both electrochemical and metallurgical factors, and it is likely that the specific way in which corrosion processes and tensile stresses interact will depend critically on the particular alloy system and environmental condition involved.

Hydrogen Embrittlement

As was shown in Figs. 1 and 2, during corrosion under acid conditions the reduction of hydrogen ions to hydrogen atoms occurs along with the production of metallic ions. These nascent hydrogen atoms can either combine to form hydrogen gas or, especially in the case of titanium and steel alloys, they can diffuse as hydrogen atoms into the metal. Certain substances, such as hydrogen sulfide, arsenic, or phosphorus compounds tend to prevent the formation of molecular hydrogen from nascent hydrogen atoms. These compounds thus tend to increase the number of nascent hydrogen atoms present on the metal surface and hence increase the fraction of the total amount of hydrogen produced by corrosion which dissolves into the metal. Applied cathodic current can also tend to encourage the accumulation of dissolved atomic hydrogen in metals. In any case, if this atomic hydrogen diffuses to internal voids it can form trapped pockets of hydrogen gas. Since molecular hydrogen cannot redissolve in the metal, a pressure of hydrogen gas is built up. These pressures can easily become great enough to rupture and distort even the strongest steel (hydrogen blistering). Even worse, in very high strength steels, the presence of dissolved hydrogen can lead to greatly reduced metal ductility (hydrogen embrittlement) and concomitant cracking. Similarly, in titanium, brittle titanium hydrides may be formed from dissolved hydrogen. These hydrides can give rise to similar embrittlement and cracking effects. The outward appearance of specimens which have cracked through hydrogen embrittlement is often very similar to that of samples which have broken through stress corrosion. Whereas, however, applied cathodic current can slow down or prevent stress corrosion, such cathodic currents will tend to increase hydrogen embrittlement by increasing the rate of hydrogen reduction.

Because it is accelerated by the presence of dissolved H_2S , hydrogen embrittlement is often a severe problem in sour oil fields. Plating operations which are generally carried out using strongly acid conditions, can also sometimes give rise to hydrogen embrittlement in steel parts if excessive plating current is applied.

Erosion Corrosion

This form of corrosion involves the acceleration and possible localization of attack due to the relative movement of a fluid environment and a metal surface. As in the case of stress corrosion, both mechanical and corrosive processes are involved. Especially susceptible metals are stainless steels and aluminum which rely for their corrosion resistance on the presence of highly protective surface films. The liquid impinging on the surface causes

a wearing away of the protective film, exposing new reactive sites which are anodic and surrounded by a relatively large cathodic area. Rapid, localized corrosion of the exposed regions can then occur. Most other metals besides stainless steels and aluminum are also susceptible. As mentioned already, the resistance of lead to sulfuric acid, for example, depends on the formation of mixed lead oxide-lead sulfate surface films. In situations where lead is exposed to turbulent dilute sulfuric acid, rapid corrosion attack can occur. In stagnant solutions of the same concentration, corrosion attack is minimal. Similarly, in desalination tube bundles, erosion corrosion may occur near the inlet end of the tubes, in the region of turbulence where the high velocity water first enters the tube bundle. Aluminum brass (by weight percent, 22Zn - 2Al - 0.065As-balance Cu) is more resistant than admiralty metal (24Zn-0.65As-balance Cu) because the presence of Al contributes to the development of a more protective and adherent surface film. Similar effects are observed for the addition of Fe to cupro-nickel. Conversely, erosion corrosion can be accelerated if the moving fluid contains abrasive particles. Erosion corrosion processes can also occur in gaseous, organic, or even liquid metal environments as well as under more familiar aqueous conditions. Both gaseous and liquid environments can combine to produce erosion corrosion. In cavitation damage, for example, large pressure changes and rapid fluid flow cause the repeated formation and collapse of bubbles at metal surfaces, thus destroying protective surface films and giving rise to concentrated localized attack.

Corrosion Fatigue

Normal fatigue is the process by which metals fail under repeated cyclic stressing, at loads which are substantially below the normal strength of the metal. The fatigue limit is the highest stress which can be cyclically applied an indefinite number of times without causing fracture. Corrosion fatigue may be defined as the combination of corrosion and normal fatigue processes leading to a reduction in fatigue resistance. This behavior is illustrated in Fig. 15, which shows the relationship between the level of applied stress and the number of cycles required to produce failure for steel. Under corrosion conditions the stress level which can be tolerated for a given number of cycles is everywhere reduced, and there no longer exists a lower stress below which failure will never occur.

As in the case of stress corrosion, corrosion fatigue processes are not well understood and can be expected to differ substantially from one alloy and corrosive environment to another. In general, however, corrosion fatigue damage can be expected to be large if the corrosive environment is one that can cause pitting. Any pits which are produced by corrosion will act as stress concentrators and thereby locally increase the effective applied cyclic stages.



FIG. 15—Schematic drawing showing the normal fatigue and corrosion fatigue behavior of steel.

Fretting Corrosion

This form of damage is usually denoted by surface discoloration and wear, as well as deep pits, in regions of slight relative (vibratory) movement between highly loaded surfaces. In fretting corrosion the slipping movements at the interface of the contacting surfaces destroy the continuity of protective surface layers, thus allowing relatively rapid attack to occur. This form of damage may be especially damaging because of resultant seizing and galling or loss of close tolerance in machine parts. Materials such as stainless steel or titanium alloys which depend critically on protective films for corrosion resistance are especially susceptible to fretting corrosion damage. Surprisingly small relative movements can give rise to fretting damage. Tomlinson, who first used the term fretting corrosion, showed that vibratory motions of as little as 8×10^{-8} cm could produce fretting damage [15,16].

In the case of the fretting corrosion of steel on steel, it has been shown that only oxygen and not moisture is required to produce damage [17]. Also, the rate of damage is decreased by moisture, an effect first noticed from the difference in weight loss observed for tests made during winter and summer. An aqueous corrosion process is therefore apparently not involved. Instead, damage results from the localized abrasion of metal to form oxide with subsequent acceleration of damage due to both the greater volume of the oxide (relative to the metal from which it formed) and the abrasive nature of the oxide particles. In this case, the effect of water in decreasing damage may be due to a lubrication effect. As might be expected, fretting damage can be decreased through the use of either solid or liquid lubricants as well as by the use of soft metal or other coatings which can exclude oxygen from the faying surfaces. Although the mechanism of fretting damage is not entirely understood, it would appear to be more related to low temperature oxidation than aqueous corrosion processes.

Other oxidation processes can lead to corrosion damage, particularly at high temperature as discussed next.

High Temperature Oxidation

The direct combination of a metal with oxidizing agents such as sulfur dioxide or oxygen is termed high temperature oxidation or, alternatively, dry corrosion. The forms which such attack can take are in many cases the same as those which occur under aqueous conditions at ambient temperatures. That is, attack may be uniform or localized and produce a variety of morphological features, including pits, preferred grain boundary attack, and selective leaching.

In high temperature oxidation, the physical and electrical properties of the corrosion product films that are formed determine the severity and extent of attack. If, for example, the oxide which forms is cracked or spalls, so that access of the oxidizing agent to the metal is unimpeded, then corrosion will continue at a constant rate. In a very early investigation of oxidation corrosion, Pilling and Bedworth proposed that oxide protectiveness was linked to the ratio of the relative volume of oxide produced to that of metal consumed [18]

$$R = \frac{Md}{mDa}$$

where a is the number of metal atoms per oxide molecule, M and m are the molecular weights of the oxide and metal, respectively, and D and d are their densities. If this value is either less than unity or substantially greater than unity, then the oxide will be unprotective. This is so because if R is less than unity, insufficient oxide volume will be produced to give complete coverage while the case of R greater than unity will give rise to cracking or spalling. In either case, the gaseous oxygen can continue to react with the metal surface as shown in Fig. 16a. In general there is only qualitative agreement with the Pilling-Bedworth rule, since other factors are important as well. As was aqueous corrosion, high temperature oxidation is an electrochemical process. That is, to form the oxide, metal atoms (M) must be increased in oxidation state while some other species, for example, O_2 , is reduced in oxidation state. That is, the two partial reactions may be written as

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

and




$$\frac{n}{4}$$
 O₂ + ne⁻ $\rightarrow \frac{n}{2}$ O⁻²

which combines to give

$$M + \frac{n}{4} \mathcal{O}_2 \to M\left(\mathcal{O} \; \frac{n}{2}\right)$$

Thus as in aqueous corrosion, high temperature oxidation consists of an oxidation reaction occurring together with a reduction reaction. For these reactions to proceed both ionic and electronic migration through the oxide film is required. As shown in Fig. 16b, if the rate of oxygen ion diffusion through the oxide film is limiting, then oxide growth occurs near the oxide environment interface. If, on the other hand, metal ion diffusion is slow, then oxide growth occurs near the metal-oxide interface, as shown in Fig. 16c. The reaction site may also be inside the oxide film if neither metal nor oxygen diffusion is limiting (Fig. 16d).

In all cases except that shown in Fig. 16*a*, the rate of oxidation will depend upon both the electronic as well as the ionic conductivity of the growing oxide film. Since the time required for both electrons and ions to pass through the film will be proportional to the film thickness, the rate of film growth in such a case will be inversely proportional to film thickness. That is, the mass of the oxide layer will increase as the square root of exposure time (parabolic growth). If the oxide film does not conduct electrons, ionic diffusion will be inhibited, leading to a slower growth rate and an oxide weight which increases with the logarithm of exposure time. A similar slow growth rate situation occurs if the oxide being formed conducts electrons but not ions.

To be protective, an oxide should be nonvolatile and nonreactive with its environment. At high temperature, the oxides which form on tungsten, for example, evaporate as they are being formed and so oxidation continues unchecked. Accelerated or catastrophic oxidation can also occur through the interaction of an oxide scale with contaminants in the oxidizing environment. The presence of vanadium in oil, for example, can lead to greatly increased oxidation rates for steel in contact with the flue gas produced when this oil is burned. V_2O_5 forms a low melting (635 C) eutectic with Fe₂O₃, whose melting point normally is 1565 C. In addition V_2O_5 is a catalyst for converting SO₂ to SO₃ and this can result in the incorporation of damaging sulfate ions into the growing oxide scale.

Environmental control, alloying, and protective coating have all been used to decrease corrosion losses through oxidation. Furnaces using molybdenum windings, for example, may be used to produce temperatures up to 1500 C or higher provided these windings are protected by an atmosphere of hydrogen. Iron-chromium-aluminum alloys may be heated for long periods in air at up to 1300 C whereas normal low carbon steel will oxidize at a rate of more than ten mdd at a temperature of less than 1000 C [19]. The use of many refractory metal alloys in high temperature applications would not be possible without the use of coatings such as fused silicides

Bacteriological Influences

Several types of bacteria are known which can cause or accelerate corrosive attack on metals. In anerobic soils a type of bacteria called Desulphovibrio desulphuricans can reduce $SO_4^{=}$ ions to $S^{=}$ ions, with the release of oxygen. This oxygen, as we have seen, can accelerate the cathodic reaction. Alternatively, the S⁼ ions can react with Fe⁺⁺ ions, thus also depolarizing the anodic reaction in iron or steel corrosion. In this way, corrosive attack instead of being slowed by the anerobic condition can continue apace. The resulting corrosion product, rather than rust, is black ferrous sulfide. This form of attack can often occur beneath asphaltic coatings on pipeline and is particularly dangerous since the outer asphalt layer shields the pipe from the applied cathodic protection current while also providing anerobic and sulfur-rich conditions. Bacteriologists have identified many different species within the genus desulphovibrio, some of which are strictly limited to salt water, and reviews of their behavior in corrosion situations are available [20,21]. Another form of microbial corrosion involves the fungus Cladosporium resinae, which has the ability to degrade the hydrocarbon found in jet fuel. Growth is controlled mainly by temperature and the availability of water. These fungi produce a wide variety of organic acids as waste products and very acidic conditions can develop beneath growing colonies. In addition a highly anerobic condition is to be expected beneath such a colony, and can lead to oxygen concentration cell corrosion. This form of corrosive attack has only come into importance with the replacement of piston powered aircraft by jet aircraft, since these fungi grow preferentially in kerosene as opposed to gasoline.

Methods of Corrosion Prevention and Control

In the previous sections the basic electrochemical principles which determine corrosion processes have been outlined and a discussion given of some of the specific forms which these processes can take. This section now reviews the principal general methods which can be taken to decrease or eliminate corrosion damage.

There are many different approaches to the prevention of corrosion. Substitute materials may be considered in place of originally chosen alloys which cannot withstand environmental effects. Alternatively, the environment may be made less aggressive through the use of inhibitors, excluded entirely by means of paint or other coatings, or altered in pH, dissolved air content, or state of agitation. Equipment design can also be changed to minimize crevice formation, water accumulation or other features which may aggravate corrosive damage. Electrochemical methods too are available which can either prevent corrosion entirely or greatly reduce its rate. In what follows, the general principles of these basic approaches to corrosion control will be outlined as an introduction to the discussion in subsequent chapters of the detailed application of such methods in industrial situations.

Protective Coatings

The use of protective coatings is probably the most common means used for retarding or preventing corrosion damage. In general, such coatings can be classified into one of three groups: (1) organic and paint coatings; (2) metallic and nonmetallic inorganic coatings; and (3) chemical conversion and anodic coatings.

Organic coatings are used primarily to protect metal parts, equipment, and structures from corrosion in the atmosphere, soil, or water. Their principal action is as physical barriers to the environment. They may contain, in addition, however, active pigments or other ingredients which affect surface pH or which cause surface passivation. Such coatings include paints, varnishes, enamels, and lacquers, as well as dipped, sprayed, or baked-on plastic, rubber, or bituminous materials. Organic coatings may often contain volatile ingredients which act simply as solvents and diluents. The service life of such coatings depends principally on the durability of the coating material itself and the adherence of this coating to the surface to be protected. This latter factor can in turn depend critically on the method of application as well as on the preparation given to the metal surface before application. Surfaces to be coated should, of course, be as free as possible from dirt, grease, scale, and initial corrosion products.

It is always advantageous to understand the true causes of corrosive action when taking corrective measures. In galvanic corrosion, for example, the intuitive approach would call for coating the obviously corroding surface. If this is done, however, the result will be to stimulate localized corrosive action at any holidays or other discontinuities which may exist in this coating. This stimulation of corrosion occurs because coating only the more active (less noble) surface produces a large cathode—small anode corrosion cell situation. Concomitant accelerated attack is therefore produced on any residual exposed anodic sites. It would be far better to coat both surfaces or alternatively only the cathodic (more noble) surface. Coating the more noble metal surface cathodically limits corrosive cell action and in addition slows the overall rate of attack since the available cathodic corrosion current is distributed over a large anodic area.

Many paint or other organic coatings systems consist of multiple coating layers each of which possesses a specialized function. Primer coatings, for example, usually provide adhesion to the metal surface for subsequent finish coatings. This adhesion may be improved by prior chemical or anodic surface treatments. Aluminum may be given a thin adherent phosphate coating, as described below, which can greatly improve the adhesion of the primer coat. Another important function of the primer coat is as a vehicle for corrosion inhibiting agents such as red lead (Pb_3O_4), or lead and zinc chromates. The function of the top coat is principally decorative and the provision of a barrier to weather and sunlight.

Metallic coatings can be applied to both ferrous and nonferrous alloys to give increased resistance to corrosion. Such coatings can be applied by electroplating, chemical reduction, hot dipping, cladding, metal spraying, mechanical plating or other methods. Regardless of the method of application, a continuous metal coating will serve as a physical barrier to the environment until it is penetrated by corrosion or mechanical damage. When the base alloy is exposed, however, the galvanic relationship of the coating and the base alloy will determine the subsequent degree of protection provided by the coating. Coatings which are anodic to the base alloy will give protection by sacrificial corrosion. More noble coatings will accelerate corrosive action of the base metal at nicks and other holidays by providing a large cathodic surface. Despite this possibility of enhanced localized attack, many metal coatings are applied to more anodic base metals. In the case of magnesium alloys, for example, virtually all metal coatings are more noble than the base metal. In determining whether a coating will be anodic or cathodic to the base metal, the influence of the environment cannot be neglected. The electromotive force series (Table 1) shows iron to be more active than cadmium. In seawater (Table 2), however, cadmium is seen to be less noble than iron. In seawater, therefore, a thin coating of cadmium will give protection to iron exposed through small pores or abrasions. In the case of tin coatings on steel, similar effects occur. In solutions of mineral salts, tin is cathodic to iron. In most fruit acids (for example, citric) tin forms complex anions which lower the effective tin concentration. This increases tin activity so that tin becomes anodic to iron. Therefore, in fruit acids, pinholes in tin coatings on "tin cans" do not undergo the concentrated attack they would in mineral salt solutions. Instead such pinholes receive protection through the sacrificial corrosion of the thin coating. The steel is thus protected from perforation. Because of the increased corrosion which occurs at pores in coatings when a more noble metal coating is used, such noble metal coatings are usually substantially thicker than coatings of less noble materials for which minor perforation is not critical.

Nonmetallic inorganic coatings can also be applied to metals for increased corrosion and wear resistance as well as for decorative purposes. Porcelain enamel coatings, for example, are alkali-alumina borosilicate glass finishes fused to the metal surface at temperatures high enough to liquify the inorganic coating material. Most such coatings are applied to sheet metal for use in such applications as kitchen appliances. The corrosion resistances of such coatings is usually very high, but they lack ductility and can be chipped or cracked in service. In inorganic coatings of higher melting point, more refractory ceramic materials can be applied by flame spraying. In flame spraying, the coating material is first melted in a high temperature flame or electric arc and then sprayed in droplet form onto the surface to be coated. Both metals and high temperature refractory ceramics such as boron nitride and hafnium carbide, as well as combinations of such materials have been applied by flame spraying processes.

Numerous other methods for the application of both metallic and ceramic coatings are available. In diffusion coating (pack cementation coatings) the coating material, in the form of a volatile compound (usually a halide) reacts at elevated temperature with the metal surface to be coated. The halide decomposes, releasing the coating metal which subsequently diffuses into the surface. Diffusion coating processes are often called by specific names such as calorizing (aluminizing), chromizing, or siliconizing. A recent review of these and other and inorganic coatings and processes is available [22].

Protective coatings and coating treatments which serve as a base for paint or other layers can also be formed on many metals and alloys by chemical and anodic methods. Chemical coatings are also termed chemical conversion coatings because the metal surface is converted to a nonmetallic compound as a result of the treatment. For example, aluminum can be given a phosphate conversion coating by exposure to an acidic soluble phosphate salt solution which contains a complexing agent (for example, F^-) for aluminum. The aluminum metal at the surface will dissolve producing Al⁺⁺⁺ ions which are complexed to form AIF₄⁻⁻ ions by the fluoride. Concurrently, the increase of pH by the reduction of H⁺ ions causes the precipitation of a basic phosphate salt (such as zinc phosphate) at the aluminum surface, where the pH is more basic than in the bulk of the liquid. If it were not for the fluoride ions, the aluminum ions would precipitate as Al(OH)₃ producing a poorly adherent layer. Careful control of the pH of the coating bath is, therefore, necessary because if the pH is too low, no film at all will form, and if too high, the film will not adhere due to the presence of Al(OH)₃. Such coatings are often used, in the case of aluminum alloys, as a base for subsequent paint layers.

Black oxide coatings can be produced on steel and iron parts by dipping in an aqueous alkaline bath heated to 200 to 300 F. Such black oxide coatings are chiefly used as bases for the application of oils and waxes. Chromate conversion coatings can also be produced on zinc, aluminum, cadmium, and magnesium alloys. In this case adherent films containing hydrated chromium oxides are produced, which give improved corrosion resistance in a variety of environments.

Anodic films may be formed on aluminum, magnesium, zinc, copper, tin, zirconium, and niobium alloys by electrolytic oxidation. In the case of

aluminum, for example, anodized coatings are produced by making the aluminum specimen the anode in a bath of sulfuric acid. The oxide film that forms naturally on aluminum is only about 25 to 100 Å thick. When aluminum is made the anode in sulfuric acid solution, however, this oxide film can be increased to many mils in thickness, if desired. Such anodically formed films in sulfuric acid are porous but can be sealed by exposure to hot water, dichromate, or other solutions. The oxide coating itself may be clear or tinted and can also be dyed before sealing. Aluminum alloys can vary widely in composition, and these compositional differences exert a considerable influence on the anodized coating. In general, lower concentrations of alloying ingredients will give rise to more transparent oxide coatings. Alloys which contain silicon tend to assume a gun metal shade while manganese as an alloying ingredient produces a brownish color due to the presence of manganese dioxide. Besides the use of sulfuric acid as an anodizing bath, anodizing processes for aluminum involving chromic and oxalic acids are also available. Still other baths, such as boric acid or phosphate solutions, are used to produce nonporous, high electrical resistance films for use in electrolytic capacitor applications. As might be expected from the number of practical applications, the literature dealing with the anodization is immense; a critical summary of much of this work is, however, available [23].

Designing for Minimum Corrosion

It is often more economical to achieve increased protection against corrosion by improved structure design than by alternate material selection or the use of protective coatings. In spite of the almost limitless number of specific conditions of materials, structural arrangements, and corrosive environments which may arise, the thorough application of a relatively few basic principles can usually lead to substantial decreases in corrosive losses. For example, sump or other areas where moisture may be trapped in contact with metal should be eliminated either throught he use of nonreentrant designs or the incorporation of adequate drain holes. Crevices are an almost inevitable part of most engineering structures, but their detrimental influence on corrosion resistance can be minimized by provision for their drainage as well as by welding or the use of proper joint compounds, for example, red lead in the case of steel crevices. The use of dissimilar metals in structures may also be dictated by economic necessity, but these should be electrically isolated if the alloys involved are widely separated in electrochemical activity. Small anodic areas connected to large cathodic areas are especially to be avoided. Corners and surface contours should be as rounded as feasible to avoid conditions where liquids or solids can collect. In welded structures, butt-welded joints should be given preference over lap joints where possible, and the weld metal should be slightly more noble than the base metal. In systems involving liquid transport, turbulent flow and gas or air entrapment should be minimized. Designs which minimize stress concentrations can be critical in avoiding possible catastrophic failure through stress corrosion or corrosion fatigue processes. In almost all cases intelligent design coupled with a basic knowledge of corrosion processes can avoid or minimize many subsequent corrosion difficulties.

Electrochemical Protection Methods

As we have seen, the corrosion of a metal requires the transfer of electrons. Thus, when two dissimilar metals are electrically connected as shown in Fig. 2, the more reactive metal passes into solution (becomes an anode), and the electrons thus produced travel to the less reactive metal where they are used up in the reduction of some substance in the electrolyte. If the external electrical connection was broken, then both metals would begin to corrode, and both anodic and cathodic processes would occur over the surfaces of each. Thus, the electrical connection between a less noble and more noble metal leads to the decreased corrosion (that is, the protection) of the more noble sample at the expense of the increased corrosion of the less noble metal, which becomes a sacrificial anode. This effect is the basis of cathodic protection. If the ability of the less noble metal to supply electrons is sufficiently great, then the corrosion of the less noble metal can be entirely prevented. Instead of a less noble and a more noble metal electrically connected together, an external direct current source can also be used to achieve the same effect, as illustrated in Fig. 16. Here an external source of current supplies electrons through an auxiliary anode to the buried pipe, shifting its potential and preventing corrosion. These effects can be readily visualized by considering Fig. 18. If no external current is applied, the submerged or buried metal will have a potential E_z and be corroding at a rate given by $I_{\rm corr}$. If an external current of a magnitude $I_x - I_{\rm corr}$ is applied (with the polarity shown in Fig. 17), the potential of the corroding metal will shift to less noble potentials, and the rate of the anodic (corrosion) reaction will decrease to $I_{corr'}$. If a larger current, I_y , is applied the potential will shift to E_a and the anodic (corrosion) reaction will be suppressed entirely. The buried or submerged metal then cannot corrode as long as the external current is kept applied. Even larger applied cathodic currents will not be of benefit and may be harmful to amphoteric metals through the production of high alkalinity at the metal surface. Where possible, cathodic protection is usually combined with the use of protective coatings in order to decrease the magnitude of the applied current density that must be maintained in order to achieve complete protection.

The preferential use of either sacrificial anodes or an external current source will depend on the details of each given cathodic protection application. Sacrificial anodes such as special magnesium, zinc, or aluminum alloys are commonly employed in the cathodic protection of ships and



FIG. 17-Schematic diagram of the cathodic protection of a buried pipe.



FIG. 18—Evans diagram illustrating the potential changes that occur during cathodic protection.

buoys while impressed current methods are widely used to protect long underground oil, gas, and water pipelines. In general, structures can only be effectively cathodically protected if they are in open contact with an electrolyte. Thus, cathodic protection cannot readily be applied to the protection of the interior of heat exchanger tubes, because of the high electrical resistance of the electrolyte path, between the auxiliary anode and the interior walls.

Anodic protection is a relatively new electrochemical protection method which is based on the formation of protective films on certain metals by an externally applied anodic current. It is only applicable to corrosion situations where passivity can occur, as shown for example in Fig. 8 in the case of iron in nitric acid. Initially, with increasing potential the corrosion rate of the iron increases. Beyond a certain critical potential, however, the corrosion rate falls drastically due to the development on the iron of a protective, passive film. The applied anodic current density required to initiate passivity may be quite high (mA/cm^2) . Once the passive state is achieved, however, the current densities required to maintain protection can be extremely low $(\mu A/cm^2)$. Since potential is the critical factor in anodic protection, a reference electrode system is required along with an electronic device (potentiostat) which can maintain the desired potential constant by automatically increasing or decreasing the applied anodic current. Anodic protection is not as generally applicable as cathodic protection, because of the special behavior required of the metal to be protected. Its low current requirements, however, can give very great economic benefits in those situations, such as stainless steel in H₂SO₄, where the required passive behavior is observed.

Corrosion Inhibitors

Inhibitors may be defined as substances which slow down the rate of corrosion reactions when added in relatively small quantities to the corrosive environment. Some inhibitors are effective because they form a protective deposit on the corroding metal. This deposit may increase the effective electrical resistance of the corrosive environment as well as prevent the access of the environment, particularly dissolved oxygen, to the metal surface. The action of such inhibitors in decreasing the corrosion current (rate) is similar to that shown in Fig. 7c. Other inhibitors may be termed anodic or cathodic, according to whether they directly affect the anodic or the cathodic corrosion reactions. Their effect on decreasing corrosion current (rate), would be similar to that shown in Figs. 7a and 7b, respectively. If an insufficient amount of an anodic corrosion inhibitor is added, the effect may be to make corrosion worse rather than better. This can happen, because, by decreasing the ratio of anodic to cathodic areas, corrosive attack is concentrated at the remaining uninhibited anodic regions. Cathodic inhibitors are safer to use because if added in a quantity insufficient to achieve complete protection, acceleration of localized corrosive attack does not occur. A reduction in the rate of attack can also be achieved in some systems by means of passivating inhibitors or passivators. As shown in Fig. 8 the corrosion rate of iron increases with increasing potential or oxidizing power of the corrosive environment, until a certain critical value is reached, above which the corrosion rate falls drastically to low levels. Other metals and alloys, particularly stainless steels, can behave in a similar fashion. Passivators act, in effect, to drive the potential of the corroding specimen into the range in which passivity occurs as well as by adsorbing onto the surface and making the onset of passivity easier to achieve. Passivators such as chromate and nitrate anions, since they can be reduced, can passivate steel even in the absence of dissolved oxygen while phosphates and molybdates are only effective in the presence of oxygen.

Slushing compounds consist of greases, oils, or waxes which contain organic polar compounds (such as amines) which adsorb onto the surface of the metal to be protected. The adsorbed layers block the effective access of the environment to the metal surface and help prevent metal dissolution as well. Similar adsorbed layers account also for the action of inhibitors used to prevent the corrosion of metal during pickling operations aimed at removing mill or boiler scale. Typical pickling inhibitors for steel include formaldehyde, propyl sulfide, and diamyl amine.

Volatile corrosion inhibitors are substances which sublime slowly at normal temperature and inhibit atmospheric corrosion. Volatile corrosion inhibitors have been principally developed to protect steel parts from rusting during shipment and storage. They may have a detrimental effect, however, particularly on zinc, cadmium, magnesium, and lead alloys (including solders).

The concentration of inhibitor required to achieve a given level of protection is usually increased by the presence of chloride ions. Other dissolved species can also affect the action of inhibitors, and a full knowledge of the chemistry of the corrosive environment is necessary to insure the desired effectiveness of inhibitors.

It has been possible here to summarize only in brief terms the methods and techniques available for the control of corrosive damage. In the chapters which follow, the specific measures currently used to minimize corrosion losses in major industries are reviewed in depth. In each case particular emphasis is placed on standard test and evaluation procedures which have been developed to identify as well as to control corrosion damage.

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Chapter 2

Corrosion Standards and Control in the Petroleum Industry

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Petroleum refineries use water, steam, hydrogen, acids, and a variety of other corrosive materials to convert crude oil into many different products, including gasolines, lubricating oils, fuel oils, and chemical plant feedstocks. Hence, refineries have not only most of the corrosion problems encountered in the utilities and chemical industries, but a few specific problems as well.

A typical refinery consists of many large interconnected units that operate continuously for up to five years without being shut down for maintenance. Some of the units operate at such high pressures and temperatures that unexpected corrosion failures can be dangerous as well as expensive. Overall, corrosion is estimated to cost from 10 to 19 cents per 42-gallon barrel of crude processed [1].² In the United States, where refineries process about 15 million barrels per day, these costs amount to at least 1.5 million dollars per day. Worldwide, to process 42 million barrels/day the cost is about 4.2 million dollars/day, distributed among alloying, maintenance, inhibitors, inspection, equipment replacement, special safety precautions, and added insurance payments because of uncertainties in predicting corrosion. Such costs are inevitable, so a major objective of corrosion control is to incur them in the least expensive way [2].

Selection of adequate materials of construction, adjustments in process conditions, and addition of inhibitors are aimed at ensuring that each unit will operate safely for much longer than its scheduled run. Materials are selected on the basis of economic evaluations of the available alternatives [3]. Such evaluations generally dictate a minimum life of ten years for each piece of equipment, with the acceptable rate of corrosion dependent on the process conditions involved. For example, a corrosion rate of 50 mils (0.050 in.) per year may be acceptable for a low-pressure vessel that has

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² Italic numbers in brackets refer to references listed at end of this chapter.

extra thick walls as a corrosion allowance, whereas the seating surfaces of process control valves must have essentially no corrosion.

Refining conditions are tending to become more severe. The current need to eliminate sulfur from most petroleum products by high-temperature, high-pressure hydrogenation is an example. Consequently, work is continually under way to identify the major sources of corrosion and to develop standards and procedures to eliminate them or to minimize their effects. This chapter summarizes the present state of the art.

Sources of Corrosion

Corrosion in refineries results from a combination of sources related to the composition of the crude oils and to the types of materials and operating conditions required in the various refining processes. Although the thousands of available crude oils are predominantly noncorrosive hydrocarbons, they also contain varying amounts of potentially corrosive sulfur compounds, salts, water, acids, and oxygen. Figure 1 is a simplified flow diagram of a refinery illustrating most of the corrosives and the process units in which they can cause damage. Because each refinery has different crude supplies and different processing schemes, the relative significance of each corrodent varies. However, some common corrosion principles and corresponding control techniques have been developed.



S = ORGANIC SULFUR COMPOUNDS AND H2S ABOVE ABOUT 500°F

FIG. 1—Major corrodents in a petroleum refinery.



FIG. 2-Typical crude distillation unit.

Crude distillation, the first step in refining, is outlined in Fig. 2. Most crudes are washed with water to remove salts and possibly some acids. If salts, particularly $CaCl_2$ and $MgCl_2$, are left in the crude, they will hydrolyze to HCl gas in the furnace that supplies heat for the distillation [4]. This HCl, plus water vapor, accompanies the naphtha vapors emerging from the top of the distillation tower. On condensation, the HCl forms highly corrosive hydrochloric acid with the water from the crude and from the steam added to aid the distillation. Similar corrosive vapors and acid condensates containing carbon dioxide, sulfur dioxide, and hydrogen sulfide are encountered in other process unit distillation towers.

Sulfur compounds are especially troublesome because they not only cause corrosion but also can poison some of the catalysts used in refining. Hydrogen sulfide is sometimes a dissolved component of the crude oil received at the refinery. In addition, it is formed in distillation furnaces, in hydrodesulfurization units, and in hydrocrackers by decomposition of organic sulfur compounds that are also present in the crude. Both the organic sulfur [5] and the hydrogen sulfide [6] are corrosive to carbon steel above 500 F. For sulfur removal, the products or the crudes are treated catalytically with high-temperature, high-pressure hydrogen. The mixture of hydrogen sulfide and hydrogen, which is becoming more prevalent as pollution controls limit product sulfur levels, requires special precautions in alloy selection.

At high temperatures, high-pressure hydrogen diffuses into metals and can react with the carbon in steel to form methane. This reaction causes fissuring and blistering as well as decarburization of the steel, with a consequent loss in ductility. Then catastrophic failure can occur without warning and with no visible deterioration of the metal.

Hydrogen is also produced by aqueous acid corrosion at low temperatures. In this case, hydrogen atoms or ions form at the metal surface, rapidly diffuse inward, and then form hydrogen molecules at defects or dislocations within the metal. Because these molecules cannot diffuse out of the metal at low temperatures, pressures of several million psi can build up and cause cracks, blisters, and serious ruptures [7]. Figure 3 is an example of ruptured blisters on the inside walls of the tower of a vapor recovery unit. Such damage is particularly severe in the fractionation section of fluid catalytic cracking units or vapor recovery units where there are cyanides and hydrogen sulfide, both of which accelerate the diffusion of hydrogen into steel. Welds, which are often significantly stronger than the base metal, are especially susceptible to cracking from this hydrogen.

The strong acids and bases required in many of the refining processes can be particularly corrosive. These include the sulfuric and hydrofluoric acids used as alkylation catalysts, the aluminum chloride plus hydrochloric acid used as both an alkylation and an isomerization catalyst, the caustic soda used to remove entrained acids from products, and the several bases such as monoethanolamine and potassium carbonate used to remove hydrogen sulfide and carbon dioxide from fuel gases. Although the bases



FIG. 3—Ruptured hydrogen blisters on the inside wall of a catalytic cracker absorber tower.

alone are noncorrosive, the dissolution and release of the acid gases can cause severe corrosion, hydrogen blistering, and stress corrosion cracking. The amount of acid gases dissolving in the water that condenses on storage tank roofs or separates to the bottom of tanks usually determines the life of such vessels and the amount of maintenance required.

Naphthenic acids cause the type of corrosion shown in Fig. 4, but the source is often difficult to identify because the characteristic sharp-edged pits and grooves are sometimes associated with severe high-temperature sulfide corrosion [8]. Naphthenic acids are initially present in most crudes at very low concentrations. However, in the fractionation process, sufficiently high local concentrations of the acids can occur at 450 to 650 F to corrode stainless steels that normally resist sulfide corrosion. Because the metal naphthenates are soluble in oil, the scale on the corroded metal is iron sulfide, which further complicates diagnosis. There is no clear consensus on what constitutes a dangerous concentration of naphthenic acids, but Derungs [9] suggests that corrosion will occur if the neutralization number is above 0.5 mg KOH/g of crude.

Perhaps the most pervasive sources of corrosion are the large amounts of water and steam required in refineries. Cooling water, both once-through and circulating, is generally several times the volume of crude processed, and is responsible for both corrosion and scaling of piping and exchangers.



FIG. 4—Naphthenic acid corrosion of Type 410SS vacuum tower internals after 1 year at about 700 F.

Coastal refineries face the added problems of sea water corrosion in coolers.

Steam is used to heat process streams, to remove gases from hydrocarbon liquids, and to improve distillations. Low-pressure steam is usually adequate for refinery process, but often high-pressure steam is also produced to operate turbine-generators for electricity. The discharge steam goes to the process units. Because very little steam condensate is returned to the boilers, chemical treatment of the boiler feed water is more critical than in many utilities. In addition, refineries burn fuels containing many byproduct oils that are too dirty or too corrosive to sell. Thus, furnaces and flue gas venting systems require more alloying or chemical treatment than typical steam generating plants.

Setting Corrosion Standards

The petroleum refining industry cooperates with several organizations within which corrosion problems are discussed and classified to develop acceptable standards and recommended practices. Composition and physical properties of construction materials, as well as laboratory tests to evaluate metals, refinery products, corrodents, and fabrication techniques are defined to take advantage of the collective experience of many individuals and companies. The standards and recommended practices which have the most influence on refinery corrosion control are listed in the Appendix to this chapter.

The American Petroleum Institute (API) is a trade organization with many working committees charged with establishing suitable standards and recommended practices for all aspects of the petroleum industry. The physical and chemical properties of most materials of construction are defined in the API standards, and data for these standards are sometimes developed by API-sponsored research programs such as the study on hightemperature hydrogen attack at the University of Wisconsin [10]. Establishing and monitoring these research programs is primarily the responsibility of the Division of Refining Committee on Refinery Equipment with its subcommittees on Corrosion, Pressure Vessels and Tanks, Piping, and Refinery Inspection Supervisors. The Inspection Supervisors Committee is also responsible for an excellent inspection manual with a comprehensive chapter on refinery corrosion [11]. The Division of Refining Mid-Year Meeting in May has a number of symposia that include papers on the latest research in refinery corrosion. Those papers are then published in the meeting proceedings. API standards and publications are made available to everyone at a nominal price.

The National Association of Corrosion Engineers (NACE) has a number of technical committees concerned with petroleum corrosion problems. These include: NACE T-1, Corrosion Control in Petroleum Production; NACE T-5B, High Temperature Corrosion; and NACE T-8, Refining Industry Corrosion. In recent years, these committees have also produced a number of significant standards and recommended practices. Several more are in preparation. NACE also sponsors symposia on refinery corrosion, and the papers are published in its magazines, *Corrosion* and *Materials Protection*.

The American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Committee issues "codes" which define safe operating conditions for materials. These codes apply to most refinery equipment and must be considered in materials selection. New uses for materials and new materials are evaluated by the committee. Specific recommendations are published as "cases" which provide guidance for similar applications elsewhere. Several unexpected failures have helped spur research programs on the physical properties of materials sponsored jointly by ASME, the Materials Properties Council, and the American Society for Testing and Materials (ASTM).

ASTM is a comprehensive organization that covers all major industries and establishes many standard tests, including some to define the quality of both construction materials and refinery oil products. Standards of sandblasting for plant preparations have been defined and published, complete with a portfolio of color photographs, by ASTM, NACE, and the Steel Structures Painting Council (SSPC). ASTM also issues specifications for paint evaluation in laboratory tests using the Salt Spray Cabinet and Weatherometer, which are defined in ASTM Standards B 117–64 and E 42–651, respectively. ASTM G 4–68, Recommended Practices for Conducting Plant Corrosion Tests, is a basic guide for developing useful corrosion control information.

Corrosion Testing and Control

Chemical analysis of process streams and metals play an important role in corrosion control. An API survey lists 46 tests [12]. Some are general, such as pH and the composition of process, cooling, or boiler-feed waters, several are specific to petroleum refining.

Corrosion is measured in the laboratory and in operating units by coupons and electrical resistance corrosion probes. Principles for corrosion coupon exposures are outlined in ASTM G 4-68. Corrosion probes and other on-stream measurement techniques including ultrasonics [13], radiography, and sentry holes are discussed in the Handbook on Corrosion Testing and Evaluation [14]. Special couplants and instruments have been developed to permit ultrasonic measurements at elevated temperatures and to allow one man to make measurements at remote locations [15]. Linear polarization techniques have also been attempted [16], but these require careful interpretation because oil films on the electrodes can cause spurious readings.

Crude Oils

Refiners can sometimes choose from many crudes. Therefore, a crude corrosivity test is valuable to ensure that the refinery will not suffer excess corrosion from a new crude. Crude oils are analyzed primarily for salt and sulfur contents to estimate corrosivity. Because the correlations with chemical compositions have been relatively poor, tests have been devised to correlate corrosion with HCl and H_2S evolution when the crudes are heated at a controlled rate. Overhead corrosion in the crude fractionator correlates quite well with HCl evolution when the crude is heated to 650 F [17]. However, the test is extremely sensitive to the heating schedule.

The evolution of H_2S from crudes heated rapidly to 850 F correlates well with high-temperature sulfidic corrosion in crude units [18]. A similar test measuring the cumulative H_2S release when the crude is heated at 2 deg F/ min [19] gives an overall estimate of relative corrosivity and also indicates at which parts of the heating equipment corrosion is most likely to occur.

Several companies have constructed pressure equipment and pilot plants to evaluate crude corrosivity directly by using coupons or electricalresistance corrosion probes. A simple pressure bomb with a 1-mil thick carbon steel probe immersed in the crude has shown a good correlation with experience and confirmed that sulfur content alone can be very misleading as a corrosivity index for some crudes [18]. Figure 5 shows a more elaborate pilot plant [20] that simulates continuous crude distillation. This unit measures corrosivity at several locations and can be used to evaluate the effects of special additives and crude pretreatments to minimize corrosivity. It also helps select the chromium steel required to resist the sulfur compounds in a particular crude. Another pilot plant has been used to show that unexpected crude corrosivity can be due primarily to mercaptan sulfur in the crude [21].

Process conditions can be modified with alkali to prevent acid corrosion. Caustic added to crude oils before and after desalting helps suppress chloride hydrolysis and reduces corrosivity by making the hot, salt-laden desalter water alkaline. Caustic may also remove some of the naphthenic acids. Ammonium hydroxide, ammonia, monoethanolamine, diethanolamine, and morpholine are added to the overhead vapors from distillation towers to ensure that any condensed water has a pH of 5 or more. This treatment reduces corrosion and provides conditions under which corrosion inhibitors can completely stop corrosion provided the salts of the neutralization reaction do not deposit in the overhead condensers. The amount of neutralizer must be carefully controlled to avoid caustic stress cracking of steels and ammonia or amine stress corrosion cracking of copper alloys [4].

Refinery corrosion inhibitors are mostly solid, high-molecular-weight nitrogen compounds (amides, amines, imidazolines and their salts with fatty acids) dissolved in hydrocarbon solvents. They also are generally



FIG. 5-Crude unit pilot plant.

surfactants and function by forming protective films on metal surfaces. Because they are solids and because concentrated inhibitor solutions are corrosive above about 250 F, special techniques are required to physically disperse them into the mostly vaporized process streams. Inhibitor solutions are diluted with a reflux stream to spray about 5 to 20 ppm by volume of the inhibitor into the vapor [22]. The efficiency of the joint efforts of desalting, neutralizing, and injecting corrosion inhibitor can be monitored with corrosion probes or with analysis of any water condensate for dissolved metals, particularly iron and copper [4].

Corrosion control can often be attained by simple changes in operating conditions with little or no economic penalty. For example, the acid gases (HCl, H₂S, CO₂, and SO₂) are not corrosive at moderate temperatures provided there is no aqueous condensation. Consequently, raising the gas temperature, lowering pressure, and installing insulation or steam tracing equipment often can eliminate the danger that these gases will cause severe corrosion or stress corrosion cracking. In equipment with little or no process flow such as relief valves, bypass lines, and instrument lines, the accumulation of corrosive gases can be prevented by a small flow (bleed) of hot process gas or a dry purge gas.

Heat Transfer

Heat transfer has a major effect on corrosion by refinery processes during both heating and cooling. Pilot plants often have low alloy heater tubes to measure the effects of H_2S release on corrosion. Simpler devices with corrosion coupons heated with soldering irons [23] or small tubes heated with small cartridge heaters are used for testing environments at moderate temperatures and pressures.

The tubing tester shown in Fig. 6 is particularly simple and useful for evaluating heat transfer problems in cooling water or in refinery process streams. Scaling tendencies of waters and the conditions that may cause dezincification of admiralty metal (70Cu, 29Zn 1Sn) can be evaluated reproducibly with this new technique [24]. An electrical cartridge heater inside the tube supplies the heat. Metal skin temperatures are adjusted by controlling the heat input, the size of the annular space between the tube and the metal cylinder, and the thickness of the partially insulating gauze. The cylinder can also be used as an auxiliary electrode for electrochemical studies.

An older test involves circulating a hot fluid through a piece of tubing and noting the effects of such exposure [25]. This test has been used to evaluate cooling water treatments [26], but it requires a cumbersome test circuit with several automatic controls. Similar devices, with cooling fluids in the tubes have been used to evaluate the corrosivities of condensates in crude unit distillation overhead condensers [27] and in power station flue gases. A somewhat more elaborate device uses a polished steel surface to



FIG. 6-Heated tube corrosion tester.

evaluate "slushing compounds" that prevent corrosion from the condensation of moisture on steels in storage [28].

A standard heat exchanger to evaluate corrosion and fouling of steel heat transfer surfaces has been proposed by NACE T-5C [29]. Water passes at a controlled rate through the tubes while steam at a controlled pressure on the shell provides heat and the desired metal skin temperatures. The tubes are split after about a 30-day test and measurements made for both corrosion and scale deposits.

High-temperature sulfidic corrosion is extremely sensitive to temperature and so can be controlled to some extent by reducing distillation pressures and metal skin temperatures in furnaces. Metal skin temperatures depend both on heat distribution in the furnace and on the heat input required for the distillation or reaction. Proper furnace design, appropriate burner settings, and efficient combusion can eliminate most hot spots. Heat recovery is crucial in refineries so streams usually pass through several preheat exchangers before they get to the furnace. If the efficiency of these exchangers is impaired, the heat duty and tube temperature in the furnace must be increased to provide the desired process temperature. Solids entrained in the process stream, salts precipitated as the stream evaporates, or organic polymers formed in the heated oil, can foul and plug the exchangers and thereby raise metal temperatures in the exchangers as well as in the furnaces.

Antifoulants that have recently been developed for refinery processes [30] are primarily detergents and suspending agents that minimize deposit formation and sometimes poison polymerization reactions. At 5 to 50 ppm in process streams, they can minimize deposits in critical exchangers and furnaces and extend operating periods between shutdowns, reduce heating costs, and minimize corrosion. Although several laboratory tests are available for screening the many compounds available [31], field tests are still the only completely reliable method to select an additive for a particular fouling problem.

Process temperatures sometimes can be reduced to minimize corrosion, but usually this approach is impractical. Instead, by varying the feed it is often possible to locate the source of the corrodents and either modify feed preparation or eliminate that particular crude from the refinery supply. High-temperature sulfidic corrosion in hot process streams can be monitored with corrosion probes [32]. Even if there is no practical remedy, at least the probe measures corrosion without requiring that the unit be shut down. The equipment life can be estimated and a resistant alloy selected and fabricated to replace the corroded equipment quickly and economically at a shutdown scheduled before the equipment becomes defective.

H_2S-H_2

Correlations have been developed to aid in selecting alloys to resist high temperature sulfides, especially where the corrodent is primarily a mixture



FIG. 7—Carbon steel corrosion by $H_2S + H_2$ in naphtha desulfurizers.

of H_2S and hydrogen [33-36]. Corrosion rates for carbon steel in naphtha desulfurizers are summarized in Fig. 7. As shown by these isocorrosion curves, the mole percent H_2S in the process stream and the operating temperature define the expected corrosion rates. If the rate is too high for carbon steel equipment to have a useful life, the appropriate alloy can be selected by multiplying the carbon steel corrosion rate by the following factors:

C, 1⁄2 Mo	1.0
1% Cr, ½ Mo	0.957
2¼ Cr, 1 Mo	0.906
5 Cr, ½ Mo	0.804
7 Cr, 1 Mo	0.736
9 Cr, 1 Mo	0.675

Other alloys can be estimated by interpolations based on chromium alloying, which provides most of the corrosion resistance aganst high-temperature sulfides.

For gas oil desulfurizers and hydrocrackers, the naphtha desulfurizer corrosion rate estimates are multiplied by 1.896.

Above specific temperatures and below specific H_2S concentrations, the corrosion reaction reverses, that is,

$$FeS + H_2 \rightarrow Fe + H_2S$$

Under these conditions, outlined by the "no corrosion" area in Fig. 7, steels should not be corroded by H_2S . However, because corrodents other than H_2S may still attack steels, caution is advisable when selecting materials for equipment operating in this no corrosion region. In particular, alloying is often required to resist high-temperature hydrogen attack.

If corrosion is too severe for the low-alloy steels, Fig. 8 shows the appropriate stainless steels that can be selected as alternatives. In this case, the isocorrosion curves are for 18Cr, 8Ni austenitic stainless steels. Type 410 (12Cr) stainless steel corrodes approximately 6.026 times faster than the 18Cr, 8Ni alloys. Again, the corrosion rates for other high-alloy steels can be estimated by interpolation primarily on the basis of chromium alloying. There is essentially no difference between naphtha and gas oil processing units in the corrosion rates of stainless steels.



FIG. 8—18–8 stainless steel corrosion by $H_2S + H_2 + hydrocarbons$.

The data used to construct Figs. 7 and 8 were obtained by exposing coupons for at least 500 h in operating units. Pilot plants also have been used to relate corrosion to temperature, H₂S concentration, and pressure in mixtures of H₂S and hydrogen [35-39] using coupons and electrical resistance corrosion probes. Under a research project sponsored by API at The Pennsylvania State University [40], another pilot plant continually weighs the gain in weight of a corroding specimen to study the kinetics of H₂S corrosion. Similar effects of mercaptan sulfur in naphtha desulfurizer feeds have been studied using a multiple-alloy corrosion prove in a pilot plant at 650 to 750 F and 300 psig [41,42].

A novel method to study high-temperature H_2S-H_2 corrosion has been developed by Dravnieks [43]. Hydrogen is bubbled through a bath of molten sulfur at a controlled temperature, and all the sulfur vapor in the hydrogen is converted in a catalytic reactor to a controlled concentration of H_2S in hydrogen. This system eliminates the possibility of segregation of the gas mixture or loss of H_2S concentration due to reaction with oxygen in air or with the walls of a steel storage cylinder.

Naphthenic Acids

High-temperature sulfide corrosion is often blamed for equipment failures that are caused by naphthenic acids [8]. These acids corrode not only low chromium alloy steels but also Types 410 (12 Cr) and 304 (18 Cr, 8 Ni) stainless steels that normally resist sulfide corrosion. On the other hand, Type 316 (18 Cr, 10 Ni, 2 Mo) stainless steel generally resists both naphthenic acids and sulfides. Often these differences in corrosion resistance are the only means of confirming that the corrodent is naphthenic acids. Alloying is the only known way to resist naphthenic acids and sulfides at high temperatures, but the costs of the minimum alloying differ so greatly that a proper diagnosis of the corrodent is critical.

Stress Corrosion Cracking

When austenitic stainless steels are used to resist sulfides or naphthenic acids, special precautions must be taken to minimize the possibility of stress corrosion cracking by both aqueous halides [44] and moist sulfide scales containing polythionic acids [45]. Resistance of alloys to stress corrosion cracking is typically evaluated in boiling 42 percent MgCl₂ for chlorides, and in cold water saturated with SO₂ and H₂S for polythionic acids. Chemical stabilization with small amounts of titanium or niobium in the steel and thermal stabilization by specific heat treatments [45] can make the austenitic stainless steels resistant to polythionic acids but not to halides. Because stress corrosion cracking is primarily a problem when the process units are shut down, special precautions can be taken as outlined in the National Association of Corrosion Engineers Recommended Practice RP-01-70. This practice involves washing with alkaline solutions to neutralize the polythionic acids and adding nitrates to the solutions to inhibit chloride cracking.

Hydrogen at High Temperature

Steels to resist high-pressure hydrogen at elevated temperature are selected using the empirical "Nelson Curves" and the appropriate ASME Codes. The Nelson Curves are issued as a recommended practice by the API and are updated from time to time. The latest are in API Publication 961, July 1970. The ASME Boiler and Pressure Vessel Code, Section VIII, Divisions 1 and 2, provides the design limits for steels in high-temperature, high-pressure service.

Chemical analysis of metals for alloying constituents is recommended before installation of critical equipment. Until better methods have been developed for marking and segregating alloys, such a precaution will help forestall serious equipment failures. In a recent refinery construction program including several new units, 1 to 6 percent of the piping sections analyzed were found to have been made of alloys other than those specified [46].

Because of its insidious nature, hydrogen attack is difficult to detect in onstream equipment. The initial stages can only be detected by metallographic examination of samples cut from the equipment [47], whereas severe damage can be detected onstream by ultrasonic measurements [48].

Hydrogen at Low Temperatures

Low-temperature hydrogen attack is equally insidious but can usually be controlled by modifications in process conditions. Painted can tests and hydrogen probes used to evaluate process streams are described in the *Handbook of Corrosion Testing and Evaluation* [14]. Washing the proces streams with water to remove some of the corrodents or adding corrosion inhibitors can sometimes alleviate the problem.

Recommended practices have been developed by API and NACE to minimize the susceptibility of welds to cracking from low-temperature hydrogen attack. Experience indicates that a weld hardness of less than Brinell 200 is satisfactory for refinery equipment in severe environments. Welds over 200 Brinell should be given a tempering heat treatment. Research sponsored by API is in progress at Battelle Memorial Institute to better define the controlling parameters.

Other Corrodents

Refinery equipment that handles strong acids and bases requires special corrosion protection, just as in the chemical industry. Similarly, cooling water and boiler water treatments are basically the same as those in utilities practice and so will not be discussed here.

Conclusion

In conclusion, refinery corrosion control, like corrosion, is expensive. The development of effective controls requires the cooperation of many individuals with various skills. Although many standards and recommended practices have already been established, more are required. Several organizations are now working to develop and report the necessary technology and experience. Correctly diagnosing the causes of refinery corrosion and devising practical cures can save money and help insure that equipment is both safe and reliable.

APPENDIX

Corrosion Standards in the Petroleum Industry

API

Recommended Practice for Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants, API Publication 941, 1970.

Recommended Practice for Welded Plain Carbon Steel Refinery Equipment for Environmental Cracking Service, API Publication 943, 1971.

NACE

NACE Standard TM-01-69, Laboratory Corrosion Testing of Metals for the Process Industries.

Recommended Practice RP-01-69, Control of External Corrosion on Underground or Submerged Metallic Piping Systems.

Recommended Practice RP-01-70, Protection of Austenitic Stainless Steel in Refineries Against Stress Corrosion Cracking by Use of Neutralizing Solutions during Shutdown.

NACE Standard TM-01-60, Visual Standards for Surfaces of New Steel Air-Blast Cleaned with Sand Abrasive.

ASME

Boiler and Pressure Vessel Code Section I, Power Boilers
Section V, Nondestructive Examination
Section VIII, Pressure Vessels—Divisions 1 and 2
Section IX, Welding Qualifications
B31–3, Petroleum Refinery Piping

ASTM

B 117-64, Salt Spray (Fog) Testing

D 130-68, Test for Detection of Copper Corrosion from Petroleum Products, by the Copper Strip Tarnish Test

D 665-68, Test for Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water

D 1261-68, Test for Effect of Grease on Copper

D 1275-67, Test for Corrosive Sulfur in Electrical Insulating Oils

D 1743-68, Test for Rust Preventive Properties of Lubricating Greases

D 1748-70, Test for Rust Protection by Metal Preservatives in the Humidity Cabinet

D 2200-67, Pictorial Surface Preparation Standards for Painting Steel Surfaces D 2550-69T, Test for Water Separation Characteristics of Aviation Turbine Fuels

G 4-68, Recommended Practices for Conducting Plant Corrosion Tests

G 23-69, Recommended Practices for Operating Light- and Water-Exposure Apparatus (Carbon Arc Type) for Exposure of Nonmetallic Materials

SSPC

SP 8-63, Pickling

Vis 1-63T, Pictorial Surface Preparation Standards for Painting Steel Surfaces

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Chapter 3

Corrosion Standards and Control in the Gas Industry

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The natural gas industry is concerned with the production, transmission, distribution, storage, processing, and utilization of natural gas. High efficiency and safety requirements result in the need for effective corrosion control of these facilities. These facilities are subject to marine, underground, and various atmospheric and process environments. A complete description of materials and environments involved in the functions of the gas industry are too numerous to completely describe herein.

The major capital investment in the industry is in the following functional types of plants: (1) production and storage wells; (2) production and storage field piping for gathering gas from the individual wells; (3) transmission pipelines for carrying gas from production and storage sources to sales and distribution facilities; (4) compressor stations and associated facilities for maintaining or boosting pressure; (5) distribution pipelines used to deliver gas to the individual residential, commercial, and industrial users; (6) measurement and regulator stations used to measure the quantity of gas and control or reduce pressure; (7) processing equipment in the form of scrubbers and dehydrators for hydrocarbon liquids and water removal. Additionally gas heating, cooling, and odorant injection equipment is common.

Production Materials and Environments

The materials and environments unique to the production of natural gas are not substantially different from those in the Petroleum Industry. High strength steel casing and tubing common to the production wells are of the J-55, N-80 varieties and in conformance with the API 5A standards.

The most common internal corrosion problems are of the "sweet gas" and "sour gas" variety, that is, hydrogen sulfide and carbon dioxide induced.

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Gas Storage Well Materials and Environments

Gas storage well materials are generally of the same steel casing and tubing varieties described for production wells. The environment to which the internal surfaces of the casing and tubing strings are exposed is basically a clean natural gas stream in gas storage fields. Storage fields are most often established in depleted gas reservoirs. Gas is injected into the field during periods of low consumption, typically in the summer months. The gas is withdrawn during peak consumption periods in the winter months.

The internal surface corrosion problems are not as common as in the production wells. Occasionally residual cushion gases contribute CO_2 or H_2S as do natural brine waters that frequently intrude during withdrawal of gas at fast rates. The use of inhibitors is common to control such problems.

The corrosion problems on the external surfaces of the casing and tubing strings are commonly those of the galvanic soil type and occasionally of the stray current type.

Natural Gas Transmission Systems

Natural gas transmission is that part of the industry engaged in the transport of natural gas, usually from the gas producing field to remote distribution areas. The bulk of the producing areas in North America are located in the Texas-Oklahoma Panhandle; Texas-Louisiana Gulf Coast, and Offshore Gulf of Mexico; West Texas-Southeast New Mexico; Four Corners area of Utah, Colorado, New Mexico, Arizona; Appalachian area; California; Alberta Province, Canada; (and of present interest) North Slope of Alaska. It should be noted that all major production areas are remote from the industrial and population centers of the northeastern and midwestern states. Figure 1 is pipeline map of the United States which illustrates the production area and transmission pipelines.

The pipeline system usually includes a gathering system in the gas production area which with compressor, metering and gas conditioning equipment bring to the main pipeline arteries a gas suitable for transport and sale. The mainline system includes one or more large diameter (16 to 36 in.) pipelines with appropriate compressor stations at typically 80- to 100-mile spacing along the pipeline length. A lateral system with metering, pressure regulating and associated equipment completes delivery to the gas distributor.

A variety of gas dehydration, desulfurization, carbon dixoide, and solids removal equipment, and natural gasoline plants will ordinarily be associated with such systems. Compression equipment may include both centrifugal and reciprocating compressors. Compressor prime movers include two- and four-cycle engines, gas turbines and steam turbines with the use of aircraft type turbine engines in recent years. The piping varies from 0.25 in. through 36 in. with 48-in. diameter pipelines presently proposed. Control of gas flow requires the use of a large number of valves,



FIG. 1-Major United States gas fields and pipelines.

regulators, and meters, and an extensive communications system ranging from private and leased telephone lines to microwave systems.

The prevalent corrosion problems are of the galvanic and differential concentration cells common to ferrous metals in soils and natural waters with resultant pitting type corrosion. A serious problem in certan areas is the stray direct current interference problem from coal mine, street railway, and industrial use of earth grounded direct current power. More recently the development and proposed large scale use of High Voltage Direct Current (HVDC) power transmission systems is of particularly serious concern. Bacterial or microbiological corrosion although difficult to validate in specific cases is generally thought to be a serious and common contributor to the underground and natural water corrosion problems.

Stress corrosion cracking has occurred in a very few instances on external surfaces of underground gas pipelines. The actual environmental components have not been identified, however, investigators point to the probability of nitrates, carbonate, bicarbonate mixtures, and caustic environments (as part of the cathodic reactions, perhaps). Hydrogen stress cracking has been reported to occur in a few cases on external surfaces of pipelines in localized areas of extreme hardness, namely, so called "hard spots" induced during manufacture of the pipe by accidental localized quenching by water spills.

Internal blistering and cracks have occurred on production gathering pipelines where the gas had a considerable hydrogen sulfide content.

The main methods of corrosion control on underground pipelines are complete coating, cathodic protection, insulated fittings at strategic points, and mitigation of stray currents by installing control bonds to the source of the stray current. The National Association of Corrosion Engineers Recommended Practice RP-01-69, "Control of External Corrosion on Underground or Submerged Metallic Piping Systems," presents these procedures and practices that are presently in general use.

The Department of Transportation, Office of Pipeline Safety has issued minimum safety standards which contain minimum corrosion control requirements for pipeline facilities carrying natural gas, and identified as Subpart I of Part 192, Title 49, Code of Federal Regulations.

Corrosion problems in compressor station equipment is not a significant problem since water treatment and inhibition of cooling waters is normal practice.

Processing equipment such as dehydrators, gas heaters, desulfurization plants and CO_2 removal processes may be considered as a means of controlling or eliminating internal corrosion to the pipeline system. Corrosion problems in this equipment are controlled by the use of inhibitors. Corrosion coupons and equipment inspection are used to monitor corrosion rates in this equipment.

Atmospheric corrosion problems are significant in industrial areas and in

offshore and coastal facilities. Coatings, paints, and metallic coatings or cladding are used to protect against atmospheric corrosion.

Coatings on the discharge piping of compressor stations (as well as exhaust stacks) are subject to constant high temperature service. The underground discharge piping is subject to temperatures ranging from 110 to 140 F typically, and occasionally as high as 160 F. These temperatures along with soil stresses created by wetting and drying of surrounding soils make a particularly tough environmental condition for the pipeline coatings used historically and commonly result in cracking and flowing of the coatings. Electrical shorts between carrier pipe and the metallic casing used at road crossings is common although insulated spacers and casing seals are used to prevent direct metallic contact and the intrusion of water and silt. Both the high temperature service requirements of coatings and the incidence of shorted casings result in extraordinary current requirements for cathodic protection.

Steel line pipe of the API 5L and 5LX specifications is the usual pipe material. Some limited use of aluminum pipelines has been reported.

Natural Gas Distribution Systems

The transmission systems customers are largely gas distribution companies. The distribution company sells to the individual residential, commercial, and industrial user and operates a complex system of mains and service lines that range from 0.75 to 20-in. diameter. Pressure regulators, metering, odorizing equipment, along with dehydration, and gas heating equipment is associated with these systems.

Pipe materials in service consist of wrought iron, cast iron, ductile iron, copper tubing for service lines, steel, and plastic. Steel is the most common material in service along with cast iron and ductile iron in certain areas. Plastic pipe is becoming popular in the small diameters (up to 4 in.). Coiled steel tubing has also had some use in recent years.

The common corrosion types are much the same as in transmission pipelines. However, galvanic cells of the bimetal types are more prevalent due to the use of different types of pipe metal in the distribution system itself, as well as inadvertent connections to underground water piping and telephone and electrical grounds. The congestion of utility facilities within service easements and beneath city streets creates serious bimetal corrosion problems in that accidental contacts and low electrical resistance between facilities often result.

Corrosion due to road deicing salts, cinder, and septic and sewer drainage add to the natural soil corrosion problems. In mining areas the release and drainage of acid mine waters creates very severe corrosion problems. The pH of mine waters has been observed to be as low as 1.8 by the author with a pH of 3 to 3.5 commonly observed.

Industry and Related Federal Standards

The natural gas industry is actively represented in and cooperates with several committees on organizations devoted to setting standards or test methods, and conducting research programs. Those standards and practices relating to the natural gas industry are listed in Appendix A of this Chapter.

The American Gas Association, National Association of Corrosion Engineers, and the American Society of Mechanical Engineers Gas Piping Standards Committee and The American Petroleum Institute are the organizations most involved in setting industry standards relating to corrosion control. The NACE is the principal organization involved in developing recommended practices, and both NACE and ASTM are involved in arranging test programs and developing standard test methods. Additionally, the American Petroleum Institute, the Steel Structures Painting Council, the American Water Works Association and the National Association of Pipe Coating Applicators are the source of certain pipe material, coatings, and surface preparation specifications.

The Office of Pipeline Safety (OPS), Department of Transportation (DoT) has issued minimum federal safety standards for the transportation of natural gas and for pipeline facilities used for transportation. These are contained in Part 192 in Title 49, Code of Federal Regulations, Subpart I, that became effective 1 August 1971 and stipulates the minimum requirements for the protection of gas pipelines from internal and external corrosion.

American Gas Association

The AGA Operating Section has a Corrosion Committee which is responsible for assembling and disseminating information and investigating problems pertaining to the control of above and below ground corrosion on gas production, storage, transmission, and distribution systems. The Corrosion Committee is not a standards writing organization but through its normal functions acts to initiate development of corrosion standards through organizations such as ASTM, NACE, and ANSI.

Additionally, the AGA sponsors industry research projects. Presently the principal research programs in the corrosion control field are in study of stress corrosion cracking, hydrogen stress cracking, and development of new and better corrosion inspection and electrical survey methods on gas pipelines.

National Association of Corrosion Engineers

The NACE has a number of Technical Committees involved in corrosion control in the natural gas industry. The Technical Committees with major involvement are as follows: T-1, "Corrosion Control in Petroleum Production"; T-1J, "Corrosion Control for Storage Wells"; T-6, "Protective Coating and Linings"; and T-10, "Underground Corrosion Control." Group Committee T-10 is the most pertinent to the gas pipeline industry since its scope involves engineering practices for the prevention and control of corrosion on underground or submerged metallic structures. Within the T-10 Group Committee are Unit Committees devoted to interference problems, cathodic protection, protective coatings systems, materials of construction, and internal corrosion of pipelines.

American Society of Mechanical Engineers (ASME)

The ASME Gas Piping Standards Committee publishes a Guide For Gas Transmission and Distribution Piping Systems which includes the Federal Gas Pipeline Safety Standards, together with the design requirements, material references, and recommended practices of the ASME Gas Piping Standards Committee. This Committee has a subcommittee on corrosion and includes recommended practices for internal, external, and atmospheric corrosion control.

American Petroleum Institute (API)

The API has numerous working committees involved in all aspects of the petroleum industry and includes corrosion subcommittees in the Pipeline Division, Production Division, and in the Refinery Division.

American Society for Testing and Materials (ASTM)

The ASTM has numerous committees that directly affect the natural gas industry through corrosion test methods and material test methods. The most pertinent are as follows: Committee G-1 Corrosion Of Metals, Subcommittee G-01.10 Methods of Test in Soil Corrosion, Committee G-3 Deterioration of Non-Metallic Materials, Subcommittee G-3.06 Deterioration of Pipeline Coatings and Linings.

Appendix B is a compilation of test methods and recommended practices for coatings materials in the natural gas industry.

Selected Corrosion Problems

It has previously been stated that the corrosion problem on underground gas piping is typically of the normal soil corrosion type. This is complicated by the variation in materials used within the gas system, as well as interconnected and closely adjacent metals used in the electrical, water, sewage, and telephone systems. Additional complications are introduced by the various soil contaminants such as deicing salts, cinders, mine waters, septic drainage, and fertilizers.

Soil itself is a heterogeneous mixture of individual components and exhibits radical changes both with depth as well as with terrain, geological, and vegetation changes. The corrosivity depends on many factors which
include resistivity, moisture content, acidity, pH, salt content and oxygen content.

Extensive underground metal piping systems suffer to a large degree from differential aereation cells (oxygen differential) along their length and is characterized by local pitting. As a result corrosion rates determined on individual specimens or coupons in specific soil types cannot provide a realistic evaluation of the corrosion rate that exists on underground piping passing through those particular soil types. The determination of corrosivity polarization characteristics, and cathodic protection requirements are more commonly made on sections of the route rather than at local areas.

The practice today is to coat and cathodically protect all underground metallic piping at the time of installation. This is in recognition that the complex soil electrolyte corrosion rates are not readily determined on a lengthy pipeline. The long period of service required of the piping makes it unlikely that any such determinations would be of permanent value; that so called low corrosion rates cannot be tolerated over this long service period requirement; and the higher cost and impracticality of attempting to delay the installation of cathodic protection until such time as the corrosion loss has progressed to some maximum loss in wall thickness.

As a result the use of cathodic protection rectifiers has increased drastically in the past 20 years. This requires effective coordination and cooperation between the cathodic protection engineers and technicians to minimize and mitigate stray current corrosion effects that may result from these dc current sources. This is generally accomplished through regional and local coordinating committees that are sponsored by NACE. These committees vary in their formal organization and procedures however they arrange and coordinate notification procedures and cathodic protection interference testing between the various underground structure owners in their geographical area. A list of these committees is contained in Appendix C.

The test methods employed for the evaluation of the effectiveness of coatings and cathodic protection, and for determining actively corroding areas is of particular interest. The bulk of the facilities in the natural gas industry are underground or marine installations of piping, wells, and appurtenances that are not accessible for periodic inspection except at great cost. This presents a need for improved methods of detecting active corrosion, and improved methods of monitoring the effectiveness of cathodic protection systems.

Pipe to soil potential readings at various points along the piping are the normal method employed to determine if the cathodic protection level is up to some appropriate criterion such as the -0.85 V to copper-copper sulfate electrode that is most commonly used. This is generally effective and accurate, however, specific situations occur which raise questions as to its complete effectiveness in locating localized points where cathodic protection may not be effective. Marine pipelines and piping beneath concrete

and asphalt roadways cannot be tested in a practical manner using this method. In cases of coating disbondment it is postulated that the long electrical paths that result are of sufficient electrical resistance to prevent effective amounts of cathodic protection current from reaching the metallic surface areas beneath the coating. There have also been questions raised as to the validity of these potential readings made at the surface of the earth directly over the center line of the pipe in cases of large diameter pipe, namely, does this potential reading truly represent the effective potential to earth of the full circumferential surface of the pipe or does it only represent the potentials on the top quadrant of this circumference?

Existing piping that was installed previous to requiring coating and cathodic protection at the time of installation presents the real corrosion problems in that they are normally bare and may have various types of pipe joint couplings that are not electrically conductive and indeed may be intermittently conductive. This makes it extremely difficult to rely on potential survey methods that are normally used to determine cathodic and anodic areas on underground piping. The more electronegative areas on unprotected pipelines are generally identified as the corroding areas and cathodic protection is then provided for in such areas.

The above serves to point out the possible shortcomings in the present practical test method in general use. Industry research is presently concentrated on various projects that hopefully will result in more effective and accurate means of monitoring cathodic protection levels, and in detecting active corrosion or corrosion damage whether propagated in the pitting, general corrosion, or cracking mode.

Corrosion control through the use of coatings, cathodic protection, and insulation has an admirable record to date and is probably 95 percent effective in the gas industry. The above discussion is not meant to infer it is not extremely effective, but to point out the areas of field testing that have shortcomings.

Several commercial electronic tools are presently available from commercial service companies that are designed to be run internally through pipelines or well casing and detect corrosion damage. They employ eddy current and or magnetic flux leakage methods to determine loss of wall thickness or anomalous conditions on the steel surface and are capable of discriminating between external and internal corrosion and detect pits, general corrosion, and localized hard spots. The pipeline tool for large diameter can be run onstream at speeds of 5 to 10 mph and carries its own power supply which provides sufficient power for an 8-h operation. These tools are of great value, however, their shortcomings are that they provide information only on past corrosion damage and do not provide information on present corrosion rates or cathodic protection levels. They are expensive to operate and are not practically applicable to all piping.

APPENDIX A-1

Regulations, Standards, and Specifications Related to the Natural Gas Industry

Title 49 of the Code of Federal Regulations, Part 192-Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards. (11 August 1970).

Title 18 of the Code of Federal Regulations, Part 2, Par. 2.69 and Part 157, Par. 157.14—Guidelines for Natural Gas Companies in Planning, Locating, Clearing and Maintenance of Rights-of-Way and Construction of Aboveground Facilities to Aid in Recreational Values: Exhibits. (10 July 1970).

National Association of Corrosion Engineers: RP-01-69

American Petroleum Institute (API)

- 1. API Standard 5L, API Specification for Line Pipe, 1970 ed.
- 2. API Standard 5LS, API Specification for Spiral-Weld Line Pipe, 1970 ed.
- 3. API Standard 5LX, API Specification for High-Test Line Pipe, 1970 ed.
- 4. API Recommended Practice 5L1, API Recommended Practice for Railroad Transportation of Line Pipe, 1967 ed.
- 5. API Standard 5A, API Specification for Casing, Tubing, and Drill Pipe, 1968 ed.
- 6. API Standard 6A, Specification for Wellhead Equipment, 1970 ed.
- 7. API Standard 6D, Specification for Pipeline Valves, 1968 ed.
- 8. API Standard 1104, Standard for Welding Pipelines and Related Facilities, 1968 ed.

The American Society for Testing and Materials (ASTM)

- 1. ASTM Specification for Welded and Seamless Steel Pipe, A 53-71.
- 2. ASTM Specification for Welded Wrought-Iron Pipe, A 72-68.
- 3. ASTM Specification for Seamless Carbon Steel Pipe for High-Temperature Service, A 106–68.
- 4. ASTM Specification for Electric-Fusion (Arc)-Welded Steel Plate Pipe (Sizes 16 in. and Over), A 134–68.
- 5. ASTM Specification for Electric-Resistance-Welded Steel Pipe, A 135-69.
- 6. ASTM Specification for Electric-Fusion (Arc)-Welded Steel Pipe (Sizes 4 in. and Over), A 139–71.
- 7. ASTM Specification for Electric-Fusion-Welded Steel Pipe for High-Pressure Service, A 155-71.
- 8. ASTM Specification for Spiral Welded Steel or Iron Pipe, A 211-68.
- 9. ASTM Specification for Seamless and Welded Steel Pipe for Low-Temperature Service, A 333-67.
- 10. ASTM Specification for Metal-Arc-Welded Steel Pipe for High-Pressure Transmission Service, A 381-71.
- 11. ASTM Specification for Electric-Resistance-Welded Coiled Steel Tubing for Gas and Fuel Oil Lines, A 539–71.
- 12. ASTM Specification for Thermoplastic Gas Pressure Pipe, Tubing, and Fittings, D 2513-70.
- 13. ASTM Specification for Reinforced Thermosetting Plastic Gas Pressure Piping and Fittings, D 2517-67.
- 14. ASTM Specification for Carbon and Alloy Steel Forgings for Pressure Vessel Shells, A 372–71.
- 15. ASTM Sampling of Natural Gas, D 1145-53.
- ASTM Test for Calorific Value of Gaseous Fuels by the Water-Flow Calorimeter, D 900–55.

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The American National Standards Institute, Inc. (ANSI)

- 1. ANSI B16.1, Cast Iron Pipe Flanges and Flanged Fittings, (B16.1-1967).
- 2. ANSI B16.5, Steel Pipe Flanges and Flanged Fittings, (B16.5-1968).
- 3. ANSI B31.8, Gas Transmission and Distribution Piping Systems, (B31.8-1968).
- 4. ANSI B36.10, Wrought-Steel and Wrought-Iron Pipe, (B36.10-1959).
- ANSI Z21.30, Installation of Gas Appliances and Gas Piping, (Z21.30– 1964).
- 6. ANSI C1, National Electrical Code, 1968, (C1-1968).

The American Society of Mechanical Engineers (ASME)

- 1. ASME Boiler and Pressure Vessel Code, Section VIII, "Pressure Vessels, Division 1," 1968.
- ASME Boiler and Pressure Vessel Code, Section IX, "Welding Qualifications," 1968.

Manufacturer's Standardization Society of the Valve and Fittings Industry

- 1. MSS SP-25, Standard Marking System for Valves, Fittings, Flanges, and Unions, 1964.
- 2. MSS SP-44, Steel Pipe Line Flanges, 1955 ed.
- 3. MSS SP-52, Cast Iron Pipe Line Valves, 1957 ed.

National Fire Protection Association (NFPA)

- 1. NFPA Standard 30, Flammable and Combustible Liquids Code, 1969 ed.
- 2. NFPA Standard 54, Installation of Gas Appliances, Gas Piping, 1969 ed.
- 3. NFPA Standard 58 Storage and Handling, Liquefield Petroleum Gases. 1969 ed.
- 4. NFPA Standard 59, LP Gases at Utility Gas Plants, 1969.

APPENDIX A-2

Regulations, Standards and Specifications Relating to the Natural Gas Industry

Structural Materials			
Brass (rods and bars for structural use)	ASTM	В	21
Bronze (manganese bronze castings)	ASTM	В	132
Carbon-steel plates	ASTM	Α	285
Cast iron (ordinary gray-iron castings)	ASTM	Α	48
Chains	ASTM	Α	56
Copper (wrought and copper alloy) rod, bar and shapes	ASTM	В	245
High-strength low-alloy structural manganese-vanadium steel	ASTM	Α	441
High-tensile carbon-silicon steel plates	ASTM	Α	212
Low-alloy structural steel	ASTM	Α	242
Manganese-vanadium steel plates	ASTM	Α	225
Malleable-iron castings	ASTM	Α	47
Plates (carbon-steel with imporved transition properties)	ASTM	Α	442
Springs, helical (for use on spring hangers	ASTM	Α	125
Steel, structural	ASTM	Α	7
Steel, structural	ASTM	Α	36
Steel, structural bars	ASTM	Α	29
Steel, structural (plates)	ASTM	Α	283
Steel, structural plates, intermediate and high temperature	ASTM	Α	515
service			
Steel, structural plates, medium and low temperature service	ASTM	Α	516
Steel, structural rivets	ASTM	Α	502

Wrought iron (plates) Wrought iron (extra-refined bars)	ASTM ASTM	A A	42 84
Fittings, Valves, and Flanges			
Brass castings	ASTM	в	62
Bronze castings	ASTM	Ř	61
Cast-iron castings	ASTM	Ā	126
	ANSI	Δ	21 10
	ANSI	Å	21.10
	AWWA	Ċ	100
Cast nodular iron for pressure-containing parts for use at elevated temperatures	ASTM	Ă	395
Ferritic nodular iron castings for valves, flanges, pipe fittings, and other piping components	ASTM	A	445
Malleable iron for castings	ASTM	Α	197
Plastic (thermoplastic) tubing pipe and fittings	ASTM	D	2513
Plastic (thermosetting) pipe and tubing	ASTM	D	2517
Steel (alloy castings) for high-temperature service	ASTM	Α	217
Steel (low alloy) castings	ASTM	Α	487
Steel (cast-carbon) for fusion welding for high-temperature service	ASTM	A	216
Steel (forged or rolled) for high-temperature service	ASTM	Α	105
Steel (forged or rolled) for general service	ASTM	Α	181
Steel (forged or rolled alloy) for high-temperature service	ASTM	Α	82
Steel (forged or rolled) low temperature service	ASTM	Α	350
Steel (factory-made wrought carbon steel and ferritic-alloy steel welding fittings)	ASTM	A	234
Steel (wrought carbon and alloy) low temperature service	ASTM	Α	420
Steel pipe flanges	AWWA	С	207
Bolting			
Steel (alloy) for high-temperature service	ASTM	Α	193
Steel (alloy) bolting materials for low-temperature service	ASTM	Α	320
Steel (carbon and alloy) for nuts	ASTM	Α	194
Steel (carbon) bars	ASTM	Α	107
Steel machine bolts and nuts (grade B)	ASTM	A	307
Steel (quenched-and-tempered alloy) bolts and studs with suitable nuts	ASTM	Α	354
Steel (quenched-and-tempered) bolts and studs	ASTM	Α	449
ripe and Tubing			
Brass (seamless) pipe	ASTM	В	43
Carbon and alloy steel forgings for pressure vessel shells	ASTM	Α	372
Cast-iron pressure pipe	ASTM	Α	377
Cast-iron (centrifugally-case) pipe	USAS	Α	21.7
	USAS	Α	21.9
Cast-iron (pit-cast) pipe	USAS	Α	21.3
Copper and copper alloy, pipe and tube	ASTM	Α	251
Copper (seamless) pipe	ASTM	B	42
Copper (seamless) tubing	ASTM	B	75
Copper (seamless) oright-annealed tubing	ASTM	B	68
Copper (seamless) water tubing	ASTM	B	88
Ducine-iron (centrilugally cast) pipe	ANSI	Α	21.52

Plastic (thermoplastic) tubing pipe and fittings	ASTM	D	2513
Plastic (thermosetting) pipe and tubing	ASTM	D	2517
Steel (electric-fusion-welded) 18-in. and larger pipe	ASTM	Α	155
for high-temperature and high-pressure service			
Steel (electric-resistance-welded) coiled tubing	ASTM	Α	539
Steel (electric-resistance-welded) pipe	ASTM	Α	135
Steel (electric-fusion-welded) pipe	ASTM	Α	139
Steel (electric-fusion-welded) large-size pipe	ASTM	Α	134
Steel (metal-arc-welded) pipe for high-pressure transmission	ASTM	Α	381
service			
Steel and iron (seamless and welded) line pipe	API		5L
Steel (seamless and welded) high-test line pipe	API		5LX
Steel (seamless and welded) casing, tubing and drill pipe	API		5A
Steel (seamless) pipe for high-temperature service	ASTM	Α	106
Steel, seamless and welded for low temperature service	ASTM	Α	333
Steel (spiral-welded) line pipe	API		5LS
Steel or iron (spiral-welded) pipe	ASTM	Α	211
Steel (welded and seamless) pipe for ordinary uses	ASTM	Α	120
Steel (welded and seamless) pipe for coiling and bending	ASTM	Α	53

APPENDIX A-3

A 225-71	tions	ecificat	ASTM Sp	
A 234-71	285-70a	A	A 6-71	
A 242-70a	307-68	Α	A 20-71	
A 283-70a	320-70	Α	A 29-67	
	333-70a	Α	A 36-70a	
MSS Stan	350-65	Α	A 42-66	
1155 Siun SD	354-66	Α	A 47-68	
SP-	372-71	Α	A 48-64	
5r	377-66	Α	A 53-71	
SP-	381-71	Α	A 56-68	
5P-4	395-70	Α	A 72-68	
SP-4	420-71	Α	A 84-68	
SP-4	441-70a	Α	A 105-68	
SP-	442-71	Α	A 106-68	
SP-	445-70	Α	A 120-69	
SP-	449-68	Α	A 125-65	
5P-0	487-71	Α	A 126-66	
American Insu	502-65	Α	A 134-68	
SIB No	515-71	Α	A 135-69	
ANSI	516-71	Α	A 139-71	
A21.	539-71	Α	A 155-71	
A21.	21-66a	В	A 181-68	
A21.	42-71	В	A 182-71	
A21.	43-70	В	A 193-71	
A21.	61-70	В	A 194-69	
A21.	62-70	В	A 197-47	
A21.	68-70	В	A 211-68	
B1.	75-71	В	A 216-70a	
B2.	88-71	В	A 217-70a	

A 225-71	B 132-70
A 234-71	B 249-71a
A 242-70a	B 251-71
A 283-70a	D 2513-70
	D 2517-67

MSS Standard Practices

SP- 6-1963
SP-25-1964
SP-44-1955
SP-46-1955
SP-47-1956
SP-48-1969
SP-52-1957
SP-55-1961
SP-61-1961
SP-63-1967

American Insurance Association

B2.2-1968		AWWA Standard
B16.1-1967		AWWA C100-55
B16.3-1963		AWWA C207-55
B16.4-1963		
B16.5-1968		NFPA Publications
B16.9-1964	1	No. 10-1962 + 1963 Adm.
B16.11-1966	1	No. 30-1963
B16.18a-1967	j	No. 58-1963
B16.20-1963	ן	No. 59-1962 + 1963 Adm.
B16.24-1962		
B16.25-1964		National Association of
B18.2.1-1966		Corrosion Engineers
B18.2.2-1966		NACE RP-01-69
B31.1.0-1967		
B31.4-1966		API Standards
B36.10-1959	5A	29th ed1968
C1-1968	5B	7th ed1968 and Suppl. 1, 1969
Z21.30-1964	5L	24th ed1969
ASME Codes	5LS	4th ed1969
ASME Doiler and Pressure Vessel	5LX	16th ed1969
Code 1968	6A	6th ed1968 and Supp. 1, 1969
Code, 1700	6D	12th ed1968 and Supp. 1, 1969
AWS Standard	1104	11th ed1968
AWS A3.0-1969		

APPENDIX B

Test Methods, Recommended Practices for Coatings, Materials in the Gas Industry

Standard for Coal-Tar Enamel Protective Coatings for Steel Water Pipe-AWWA-C203	AWWA 8310-D Committee
Coal-Tar Coatings for Underground Use	NACE
Synthetic Resin Primer for Coal-Tar Enamel, Research Report 8, U.S. Dept. of the Interior,	U.S. Government Printing Office
Bureau of Reclamation	
Asphalt Type Protective Coatings for Underground	NACE
Pipelines-Mastic Systems	
Asphalt Type Protective Coatings for Underground	NACE
Pipelines-Wrapped Systems	
Asphalt Protective Coatings for Pipelines-Construc-	The Asphalt Institute
tion Series No. 96—Wrapped and Mastic Systems	
Asphalt Type Protective Coatings for Underground	NACE
Pipelines	/
Hot-Applied Wax Type Protective Coatings and Wrappers for Underground Pipelines	NACE
Prefabricated Plastic Films for Pipeline Coatings	NACE
"Control of Pipeline Corrosion," pp. 9-18, A. W.	NACE
Peabody, Dec. 1967	
Recommended Practices Associated with the Appli- cation of Organic Coatings to the External Surface	NACE
Methods of Measuring Leakage Conductance of Coating on Buried or Submerged Pipelines	NACE

Inspection of Pipeline Coatings	NACE
Nondestructive Measurement of Film Thickness of Pipeline Coatings on Steel	ASTM G 12-69T
Test for Cathodic Disbonding of Pipeline Coatings	ASTM G 8–69T
Test for Water Penetration into Pipeline Coatings	ASTM G 9-69T
Test for Rockwell Hardness of Plastics and Electric Insulating Materials	ASTM D 785–65
Test for Penetration of Bituminous Materials	ASTM D 5–65
Test for Indentation Hardness of Rubber and Plastics by Means of a Durometer	ASTM D 2240-68
Test for Shrinkage Factors of Soils	ASTM D 427-61
Test for Resistance of Plastics to Chemical Reagents	ASTM D 543-67
Test Method of Resistance of Plastics to Chemical Reagents, Federal Test Standard No. 406, Method 7011	General Services Adm.
Thermal Evaluation of Rigid Electrical Insulating Materials	ASTM D 2304-68
Recommended Practice for Determining the Effect of Overbaking an Organic Coatings	ASTM D 2454–68
Test for Coatings Designed to be Resistant to Ele- vated Temperatures During Their Service Life	ASTM D 2485-68
Recommended Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi	ASTM G 21-70
Test Method for Mildew Resistance of Plastics by Mixed Culture Method, Agar Medium, Federal Test Standard No. 406, Method 6091	General Services Adm.
Military Specification and Test Method for Fungus Resistance, MIL-F-8261A (WSAF)	U.S. Naval Publication
Method of Test for Effects of Outdoor Weathering on Pipeline Coating	ASTM G 11-69T
Test for Abrasion Resistance of Pipeline Coatings	ASTM G 669T
Test for Bendability of Pipeline Coatings	ASTM G 10-68T
Test for Adhesion of Organic Coatings	ASTM D 2197-68
Test for Impact Resistance of Pipeline Coatings (Limestone Drop Test)	ASTM G 13-69T
Test for Impact Resistance of Pipeline Coatings (Falling Weight Test)	ASTM G 14-69T
Recommended Practice for Internal Coating of Line Pipe	API RP5L2

APPENDIX C

Corrosion Interference Coordinating Committees

Arizona Corrosion Correlating Council Baltimore-Washington Electrolysis Committee Birmingham Electrolysis Committee Central California Cathodic Protection Committee Central Ohio Corrosion Coordinating Committee Chicago Area Joint Electrolysis Committee Chicago Region Committee on Underground Corrosion Cleveland Committee on Corrosion Columbus and Central Ohio Committee on Corrosion Connecticut Committee on Corrosion **C**orpus Christi Coordinating Committee Corrosion Subcommittee of Kentucky Gas Association Dade County Utilities (Florida) Dayton, Ohio Corrosion Committee Denver Metropolitan Committee on Corrosion (not active) Des Moines Electrolysis Committee Detroit and Michigan Committee on Electrolysis East Bay Electrolysis Coordinating Committee (Oakland, Calif.) Eastern Montreal Electrolysis Committee Eastern New York Corrosion Coordinating Committee Eastern Ohio Corrosion Coordinating Committee Eastern Pennsylvania Corrosion Committee El Paso Area Corrosion Correlating Committee Flagstaff, Arizona Underground Corrosion Correlating Committee Greater Boston Electrolysis Committee Greater Indiana Corrosion Committee Greater New York Committee on Corrosion Illinois-St. Louis Committee on Underground Corrosion Indianapolis Committee on Corrosion Joint Committee for the Protection of Underground Structures in Alameda and Contra Costa Counties (California) Kentucky Corrosion Coordinating Committee (Kentucky Gas Association) Lafayette, Louisiana Underground Corrosion Correlating Committee Los Angeles, California Underground Corrosion Correlating Committee Louisiana Coordinating Committee Louisville Electrolysis Committee Massachusetts Committee on Corrosion Milwaukee Area Corrosion Committee New Jersey Committee on Corrosion Northeastern Ohio Corrosion Coordinating Committee Northwest Electrolysis Coordinating Committee (San Francisco) Northwest Electrolysis Coordinating Council (Oregon/Washington) Northwest Pacific Electrolysis Coordinating Council (Vancouver, B.C.) Northwest Pipe Line Operators (Oregon/(Washington) **Ok-Ark-La-Tex Corrosion Committee** Omaha and Council Bluffs Electrolysis Committee Oregon Corrosion Committee, Dallas Pacific Coast Gas Association Corrosion Mitigation Committee Philadelphia Electrolysis Committee Pittsburgh Public Service Coordination Committee Public Utilities Commission Corrosion Committee (Ontario, Canada) San Diego County Underground Corrosion Committee (California) San Francisco Electrolysis Committee Southern California Cathodic Protection Committee Southern Idaho-Eastern Oregon Underground Corrosion Committee Southern Ontario Council on Electrolysis Northern Technical Committee Western and Central Committee Southern West Virginia Corrosion Coordinating Committee South Florida Corrosion Council Southwest British Columbia Electrolysis Coordinating Council St. Louis, Missouri Underground Corrosion Correlating Committee Toledo and Northwestern Ohio Committee on Corrosion

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Western Inter-Utility HVDC Committee for Earth Current and Inductive Coordination Studies
Western New York State Corrosion Committee
Western Ohio Corrosion Coordinating Committee
Western Pennsylvania Corrosion Coordinating Committee
Wyoming Underground Corrosion Coordinating Committee

APPENDIX D

Societies with Interests in Corrosion Control in the Gas Industry American Gas Association 605 Third Ave. New York, N.Y. 10016 American Institute of Chemical Engineers (AICHhE) 345 East 47th St. New York, N.Y. 10017 American Institute of Chemists 79 Madison Ave. New York, N.Y. 10016 American Institute of Consulting Engineers (AICE) 345 East 47th St. New York, N.Y. 10017 American Institute of Industrial Engineers (AIIE) 345 East 47th St. New York, N.Y. 10017 American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME), 345 East 47th St. New York, N.Y. 10017 American Petroleum Institute (API) 1271 Avenue of the Americas New York, N.Y. 10020 American Railway Engineering Association 59 East Van Buren St. Chicago, Ill. 60605 American Society of Civil Engineers (ASCE) Pipeline Division 345 East 47th St. New York, N.Y. 10017 American Society of Safety Engineers (ASSE) 5 North Wabash Ave. Chicago, Ill. 60602 American Society for Metals (ASM) Metals Park. Ohio 44073 American Society for Testing and Materials (ASTM) 1916 Race St. Philadelphia, Pa. 19103 American Water Works Association 2 Park Ave. New York, N.Y. 10016

American Welding Society 345 East 47th St. New York, N.Y. 10017 Asphalt Institute, The University of Maryland College Park, Md. 20742 British Association of Corrosion Engineers London, England British Cast Iron Research Association (BCIRA) London, England British Iron and Steel Research Association (BISRA) London, England Cast Iron Pipe Research Association (CIPRA) Suite 3440, Prudential Plaza Chicago, Ill. 60601 Copper Development Association, Inc. 405 Lexington Ave. New York, N.Y. 10017 Electrochemical Society (Corrosion Division) 30 East 42nd St. New York, N.Y. 10017 Federation of Societies for Paint Technology (FSPT) 121 South Broad St. Philadelphia, Pa. 19107 Institute of Electrical and Electronics Engineers Box A, Lenox Hill Station New York, N.Y. 10021 Institute of Materials Research National Bureau of Standards Gaithersburg, Md. 20760 Manufacturers Standardization Society of the Valve and Fitting Industry 420 Lexington Ave. New York, N.Y. 10017 National Association of Corrosion Engineers (NACE) 2400 West Loop South Houston, Texas 77027 National Association of Pipe Coating Applicators 2504 Flournoy-Lucas Road Shreveport, La. 71106 Office of Pipeline Safety U.S. Department of Transportation 400 Sixth St., S.W. Washington, D.C. 20024 Petroleum Industry Research Foundation 60 East 42nd St. New York, N.Y. 10017 Pipe Line Contractors Association National Bankers Life Building 202 South Ervay Dallas, Texas 75201

Steel Structures Paint Council 4400 Fifth Ave. Pittsburgh, Pa. 00000 Society of Consulting Corrosion Engineers 205-627 Eighth Ave. Calgary 2, Canada Society for Non-Destructive Testing (SNT) 914 Chicago Ave. Evanston, Ill. 60202 Society of Petroleum Engineers of AIME 6300 North Central Expressway Dallas, Texas 75206 Society of Plastics Engineers. Inc. **65** Prospect Street Stamford, Conn. 06902 United States of America Standards Institute (formerly American Standards Association) 10 East 40th St. New York, N.Y. 10016

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Chapter 4

Corrosion Standards and Control in the Automobile Industry

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Motor vehicles, passenger cars, and trucks are used in many parts of the world. They are operated in all types of weather, parked outdoors when not in use, and thus, subjected to extremes of weather; high temperature, low temperature, rain, snow, high relative humidity, etc. They are driven over roads which have been salted for deicing or dust control purposes and parked in wet garages. Engine cooling systems, exhaust silencing and related parts, hydraulic brake mechanisms, and various lubrication systems are subjected to specific environments internally as well as the external environments noted above.

The automobile is constructed primarily of steel and cast iron, but other metals and alloys are used for specific parts. The general methods for preventing corrosion are used, namely:

- 1. Selection of a metal or alloy resistant to a specific environment.
- 2. Modifying the environment by adding corrosion inhibitors or by keeping metal surfaces dry.
- 3. Separating a corrodible metal from the environment with a protective coating such as paint or metallic coatings.
- 4. Use of sacrificial coatings or modification of electrode potential with less noble metals.

Industry Standards

Although the standards for corrosion resistance of automobiles and trucks are generally set by each manufacturer for his products, competitive pressures and common suppliers have caused a similarity in choice of materials and coatings for equivalent parts. Some differences do exist because of differences in design. The corrosion resistance standards for a specific company are based on the Society of Automotive Engineers Information Reports, Recommended Practices, and Specifications tempered by experiences of the engineers of that company.

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"Prevention of Corrosion of Metals," SAE Information Report J477a is a general discussion of corrosion and serves as a guide for automotive designers. Other recommended practices or specifications such as tests for "Motor Vehicle Lighting Devices and Components," SAE J575 and "Motor Vehicle Seat Bdlt Assemblies," SAE J4 include corrosion resistance requirements based on resistance to the neutral salt spray test. These requirements are now included in Motor Vehicle Safety Standards MVSS 108 [1]² and MVSS 209 [2] established by the National Highway Traffic Safety Administration and are exceptions to the setting of corrosion standards by each manufacturer for his products.

Corrosion Testing and Controls

Corrosion testing is similar to other test methods performed upon automotive components in that the conditions expected to be encountered in service are simulated. Normally this is difficult to accomplish in the laboratory because service environments for the automobile are complex and differ for each automobile. Corrosion testing of automobiles and automotive components, therefore, is based on an analysis of the environmental factors which may be corrosive and the selection of those factors which will affect the metals or metal systems being considered.

One of the simplest accelerated corrosion tests used in the automobile industry is the neutral salt spray test which was first formally presented by J. A. Capp in 1914 [3]. The salt spray test was widely used, even before the method was adopted by the American Society for Testing and Materials as Tentative Standard B 117 in 1939. This method of test has been refined and the control of test parameters improved at various times since it was first adopted. In 1944 the test solution was standardized at a concentration of 20 percent sodium chloride. The concentration was changed in 1953 to 5 percent sodium chloride and has remained at that percentage. The neutral salt spray test has been useful as a first approximation for the corrosion resistance of various assemblies such as exterior lamps and the protection given to exterior automobile body surfaces by various combinations of chemical surface treatments, primers, and color coatings. The test is also considered suitable for passenger compartment hardware such as that used for seat belts.

Prior to adoption as Tentative Standard B 117 in 1939, the neutral salt spray test was used for various metallic coatings such as zinc, cadmium, and decorative copper-nickel-chromium coatings, but the results of the test did not correlate well with service. Copper-nickel-chromium electrodeposits which failed early in the salt spray test would fail in service, but in many instances coatings which were reistant to the salt spray test sometimes failed in service in less time than in the salt spray test.

² Italic numbers in brackets refer to references listed at the end of this chapter.

One of the earliest modifications of the neutral salt spray test was the addition of acetic acid by C. F. Nixon [4]. This modification which was adopted by ASTM B 287 Acetic Acid Salt Spray (Fog) Test produced corrosion on copper-nickel-chromium plated zinc base die castings which resembled that found on similar parts of cars operated in Detroit. The time to produce this corrosion, however, was about 200 h, too long for use as a quality control test.

Because neither the neutral salt spray test nor the acetic acid salt spray test was considered satisfactory, the American Electroplaters' Society Research Committee sponsored Project 15 to study accelerated corrosion tests for electrodeposited metals. The method used for Project 15 illustrates how suitable accelerated corrosion tests are developed to predict the service life of automotive parts [5-11]. Project 15 was assigned to a committee composed of representatives from the major automobile companies, suppliers of plated parts, and suppliers of plating chemicals. The first phase of the project was to establish goals, evaluate existing tests, and measure the corrosion rate of decorative plating in Detroit by means of standard test panels attached to taxicabs. The Detroit environment was chosen because corrosion surveys indicated that automotive decorative plating deteriorated in Detroit more rapidly than in most other locations in the United States.

The second phase of the project was to analyze the environment and to determine which components were corrosive. Samples of slush were collected from city streets in test collectors mounted on cars. Samples of rainwater were also collected at stationary corrosion testing sites. Observers also noted that corrosion took place more rapidly when decorative plated parts were covered with road dirt and not washed frequently. Application of a slurry of kaolin containing various salts permitted a systematic study of the twenty metallic elements and chloride, nitrate, and sulfate anions found in the slush and rainwater collections. Copper and iron salts were found to be the most corrosive of the metallic elements present. The addition of copper nitrate and ferric chloride to sodium and ammonium chloride in a kaolin slurry resulted in Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure, ASTM B 380. Concentrations of salts in the method were selected to produce, in 20 h, the degree of corrosion observed in one year of atmospheric exposure on cars driven in Detroit.

The discovery that the addition of copper and iron salts to the kaolin slurry would greatly accelerate the corrosion of decorative chromium plated parts suggested that these ions would also accelerate the corrosion produced in the salt spray test. The addition of copper salts was found to greatly accelerate the acetic acid salt spray test and led to the development of the Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test) ASTM B 368. The CASS Test test produces, in 16 h, the same degree of corrosion as the 20-h Corrodkote test. Both of these tests were instrumental in developing a plating procedure which greatly improved the durability of decorative chromium plating on automobile parts [12,13].

A study of the mechanisms of corrosion of copper-nickel-chromium and nickel-chromium coating on steel and zinc base die castings by R. L. Saur [14] resulted in an accelerated electrolytic corrosion test (EC) which permits predicting the durability of decorative chromium plating in minutes. This test is currently being studied by ASTM Committee B 8 on Electrodeposited Coatings.

Both the CASS and Corrodkote tests have been tried on anodized aluminum as well as stainless steel, automotive trim parts with unsatisfactory results.

The FACT (Ford Anodized Aluminum Corrosion Test) Testing Method, ASTM B 538 and acid dissolution tests were developed for predicting the durability of anodized aluminum bright metal trim. The Corrodkote test does give an indication of the resistance to penetration of the anodic coating resulting in white aluminum corrosion spots but does not correlate well with service. An acid dissolution test [15] developed to correlate with the formation of an opaque white stain on the surface of the anodic coating consists of immersing a test sample cut from an anodized aluminum part in a water solution containing 20 g of chromic acid (CrO₃) and 35 ml of 85 percent orthophosphoric acid per liter at 100 deg F for 15 min. The resistance of the anodic coating to dissolution in the acid solution is considered a measure of the resistance to blooming or white staining in automotive service. This test is also being studied by ASTM Committee B 8 on Electrodeposited Coatings. A similar test using a solution of 10 g per liter of anhydrous sodium sulfite per liter with the pH adjusted to 3.75 with acetic acid and further reduced to 2.5 with sulfuric acid was also found to predict the resistance of the anodic coating on aluminum to blooming [16, 17].

Two accelerated corrosion test methods are available for stainless steel bright metal decorative trim. Both tests use a solution containing 0.5 g of sodium sulfate, 0.25 g of sodium sulfite, 0.10 g of sodium thiosulfate, 52.2 g of sodium chloride and 52.5 g of calcium chloride per liter of solution adjusted to a pH of 9.3 \pm 0.05. In one method, the dip dry test [18], the samples of stainless steel are alternately immersed in the solution and heated with infrared lamps for 90 s and the cycle repeated. This test requires 4 h to produce the type of corrosion observed on automotive stainless steel trim parts. The other method [19] consists of soaking gelatin-coated photographic paper in the test solution, application of the photographic paper with the gelatin side in contact with the stainless steel test surface, enclosing the stainless steel test sample with the photographic paper in a polyethylene bag, and sealing the bag with a vapor tight seal. The sample is heated in an oven to $215 \pm 5 \deg F$ for 10 min. After removal from the oven and the plastic bag, the photographic paper is immediately removed from the test surface while still moist and immersed in a solution containing 10 g per liter of potassium ferricyanide. Corrosion products transferred to

the photographic paper are developed giving a record of the test results. Both tests simulate the type and degree of rusting observed on cars operated in western Pennsylvania where salt and cinders are used for deicing roads. The two tests aided in improving the corrosion resistance of stainless steel for automotive trim by additions of molybdenum and processing changes to eliminate surface chromium depletion.

A number of accelerated corrosion tests are available for evaluating the effectiveness of inhibitors in engine coolants. The simplest and most rapid of these is the Corrosion Test for Engine Antifreeze in Glassware, ASTM D 1384. This test is also the least reliable but is suitable for preliminary screening of inhibitors. The other methods; Simulated Service Corrosion Testing of Engine Antifreezes, ASTM D 2570, Recommended Practice for Testing Engine Antifreezes by Engine Dynamometer, ASTM D 2758, and Recommended Practice for Testing Engine Coolants in Vehicle Service, ASTM D 2847 are more sophisticated, time consuming, and progressively more reliable. Modifications of the glassware test to produce erosion of radiator brass and of the simulated service test to evaluate durability are being used [20] but these modifications have not been adopted as ASTM standard methods of tests.

Two specific corrosion tests; Test for Cavitation-Erosion Characteristics of Aluminum in Engine Antifreeze Solutions using Ultrasonic Energy, ASTM D 2966 and Test for Cavitation-Erosion Corrosion Characteristics of Aluminum Automotive Water Pumps with Coolants, ASTM D 2809 are useful in evaluating coolant formulations for use in engines having aluminum water pump components. The first of the above test methods is more rapid but less reliable than the second.

Accelerated corrosion tests to evaluate inhibitors for various fluids and lubricants used by the automobile industry simulate operation of the test component under abnormal conditions which have been found by experience to be corrosive. ASTM *STP 315* describes engine tests, one of which, Sequence II, was designed to evaluate rusting and corrosion as well as scuffing, wear and sludge and varnish deposition. In this test the coolant temperature is purposely controlled to produce condensation of combustion products which mix with the lubricant causing corrosion and rusting of parts unless the lubricant contains suitable inhibitors. The operating sequence simulates frequent short-trip type of operation.

Other standard tests used for evaluation of automotive lubricants are: Test for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test, ASTM D 130; Test for Rust Preventing Characteristics of Steam Turbine Oils in the Presence of Water, ASTM D 665; Test for Rust Preventive Properties of Lubricating Greases, ASTM D 1743; and Test for Rust Protection by Metal Preservatives in the Humidity Cabinet. ASTM D 1748. ASTM D 1743 includes 1-min operation of a roller bearing to distribute the lubricating grease on to the bearing surfaces in a manner similar to that expected in an operating vehicle. The bearing is then rinsed in water and stored over water in an airtight container to simulate vehicle storage.

A form of humidity test which is frequently used to evaluate rust preventing characteristics of automatic transmission and power steering fluids is to coat steel test pieces having highly polished surfaces by immersion in the test fluid, and to suspend the test piece over water in an airtight container. Condensation is produced on the test piece by alternate heating and cooling.

Tests for corrosion inhibiting characteristics of hydraulic brake fluids are outlined in SAE Standards for Brake Fluid J1702 and J1703 published in the SAE Handbook.

As noted earlier the Salt Spray (Fog) Testing Method, ASTM B 117, is used for evaluation of automotive primers and paints. Other corrosion tests used by the automotive industry for such coatings are: Water Fog Testing of Organic Coating, ASTM D 1735; Test for Filiform Corrosion Resistance of Organic Coating, ASTM D 2803; Testing Finishes on Primed Metallic Substrates for Resistance to Humidity-Thermal Cycle Cracking ASTM D 2246; and Testing of Coated Metal Specimens at 100 percent Relative Humidity, ASTM D 2247.

Although not standardized, accelerated corrosion tests used to evaluate exhaust pipe, muffler, and tail pipe material should be mentioned while discussing automotive corrosion tests. Such tests are usually cyclic tests in which the test pieces are periodically exposed to hot engine exhaust condensate (or a very dilute solution of sulfuric and hydrobromic acids) by partial immersion followed by heating to a temperature in the range of 500 to 1000 deg F. The higher temperature is used for components located close to the engine and the lower temperature for the components farthest from the engine. The immersion in engine exhaust condensate simulates the condensation which occurs during short-trip driving and exposure to high temperature simulates the heat encountered during highway driving. The test parameters are arbitrarily chosen to suit the convenience of the laboratory doing the testing and have given reasonably good results when comparing various materials. The aforementioned test simulates the internal environment of muffler and tailpipe components. Tests for external corrosion of mufflers and tailpipes must include scaling tests conducted by heating test specimens in a furnace to the maximum expected temperature and periodically removing them from the furnace and spraying while still hot with a dilute salt solution. This test simulates operation at high speeds over salted and slushy roads.

Occasionally a test is required which will evaluate a particular property of a metal, such as susceptibility to cracking when stressed during exposure to a specific environment. An example is the observed stress corrosion cracking of brass in an atmosphere containing ammonia or organic amines. The test commonly used for evaluating the susceptibility of brass cracking is the Mercuric Nitrate Test. This test consists of immersing the brass part in a solution containing 1 percent nitric acid and 1 percent mercuric nitrate for 1 h and then examining the part for cracking. Immersion in a boiling solution of magnesium chloride is a similar type test used for stainless steel.

Exposure of test panels on outdoor static and mobile sites, although not an accelerated test, is used for evaluating exterior bright metal trim and organic automotive finishes. Static sites are primarily located in Detroit, near New York City, in Florida, and in Arizona. Mobile sites consist of racks mounted on trucks or under the bumper on passenger cars. This type of testing provides more reliable results than obtainable form accelerated corrosion tests and are less expensive and more consistent than testing on completed vehicles.

Electrochemical techniques, such as anodic and linear polarization measurements have been used to study corrosion of automobile trim materials [21,22] and to measure instantaneous corrosion rates in a simulated engine cooling system [23]. As noted earlier, an EC test was devised to test the durability of copper-nickel-chromium electrodeposits on bright metal trim. This test has been proposed and is under consideration by ASTM Committee B 8 on Electrodeposited and Related Coatings for adoption as a standard method of test. Linear polarization measurements can be used to evaluate test results in a similar manner to weight loss measurements, thickness loss measurements, or degradation of appearance.

The final test for automobile corrosion is the test of the assembled vehicle. There are probably as many variations of accelerated corrosion test procedures for the complete motor vehicle as there are project engineers supervising such tests, and variations may also be introduced because of interest in a specific component. The test procedures usually contain repeated cycles, each cycle consisting of various combinations of operation over salted gravel roads, through splash troughs containing dilute salt solutions, over rough roads, parked in humid locations, or exposed in large salt spray rooms. Such cycles are ueful for evaluating body corrosion [24,25] as well as the durability of various other components.

"An Appraisal of the Problems of Accelerated Testing for Atmospheric Corrosion" prepared by the International Electrotechnical Commission Technical Committee No. 50 Environmental Testing calls attention to many of the problems which are associated with accelerated testing for atmospheric corrosion. These problems also apply to accelerated corrosion testing for automobiles which is further complicated by variations in operation and usage. Corrosion surveys of rental cars and customers' cars in parking lots conducted annually show how well the accelerated corrosion tests predict durability.

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Chapter 5

Corrosion Standards and Control in the Pipeline Industry

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The discussion in this chapter concerns itself with any pipeline used for the transportation of materials. Materials involved can include, but are not necessarily limited to, fuel gas, petroleum and petroleum products, water, chemical solutions, effluents from manufacturing plants, and solids being transported in slurry form. Our consideration of corrosion will concern itself with external pipeline corrosion which may occur underground, in a submerged condition, or exposed to the atmosphere. Internal corrosion will be considered for those pipelines carrying material which can be expected to cause internal corrosion under specific conditions. Discussion of corrosion will concern itself with metallic pipelines as opposed to nonmetal pipelines (used in some instances) which are subject to deterioration with time rather than corrosion with time, which is taken as a function of metals only.

Upon consideration of the many materials being transported by pipeline within the pipeline industry, it can be readily understood that the amount of existing pipelines throughout the industry involves a tremendous investment in effort and capital. The magnitude of pipeline projects continues to increase. As an example of this, a single specific project in the planning stage, as this chapter is written, involves the projected construction of a major high-pressure gas pipeline from the northern coast of Alaska to the northern portion of Central United States. As an example of the magnitude of this project, the amount of steel presently planned for installation in the pipeline alone will involve on the order of 1 500 000 tons of steel. The final cost of the overall project is currently estimated at \$5 billion.

As the size of individual pipeline construction projects increases, and as their location in inaccessible areas becomes more common (such as through the Arctic wastes, or under deep marine conditions) the need for adequate corrosion control becomes more and more important. This is associated with the increasing cost of a corrosion failure in terms of cost of product

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lost and cost of effecting repairs. Further, if the failure is catastrophic in nature, the cost of interruption of pipeline throughput will be a major additional cost factor.

General

Types of Corrosion Problems Encountered

The pipeline industry is confronted with a wide range of corrosion problems. External surfaces of pipelines in contact with soils, waters, or an atmospheric environment, and the interior surfaces of pipelines which are in contact with a potentially corrosive material being carried by the pipeline, are subject to most of the basic corrosion processes and most of the forms of corrosion attack which have been covered in detai' in Chapter 1 of this book. In addition to the general applicability of basic corrosion processes and forms of attack, the pipeline industry is faced with corrosion problems which are peculiar to the industry. Some of these are discussed in detail in a later portion of this chapter.

Stray Current Corrosion-A form of corrosion attack which can occur on pipelines, but which is not covered in detail in Chapter 1, is categorized as stray current corrosion. By stray current, is meant a flow of direct current in the earth from some outside source (as opposed to corrosion current resulting from an environmental condition on the pipeline external or internal surface) which results in collection of the stray direct current by the pipeline from the earth in one area, and discharge of the current back to earth at some other area on the pipeline which may be closer to the ultimate destination of the current flow pattern. Examples of stray current sources include direct-current-operated transit systems; mining operations utilizing direct current (such as hauling equipment and mining machines); direct-current welding operations; industrial processes using direct current; and cathodic-protection systems installed on other structures (including pipelines of other ownership) for corrosion control but which may, if improperly installed, cause stray current effects upon neighboring pipelines. In addition to the man-made sources of stray current itemized, there may, under certain conditions, be a corrosive effect exercised by so-called telluric currents. Telluric currents, or earth currents, are a natural phenomenon caused by disturbances of the earth's magnetic field which result in induced direct currents on pipelines located in the areas where the magnetic disturbances occur. No matter what the source of the stray direct current may be, there is no damage, normally, where the current is picked up from the earth by the pipeline, but where this same current is discharged back to earth to continue its journey to its source, corrosion attack does occur. The magnitude of currents involved under stray directcurrent conditions can easily be far greater than currents of natural origin resulting from the corrosion processes discussed in Chapter 1, with the

result that corrosion failures can occur within a relatively short period of time.

The above discussion has been directed toward the corrosive effects of stray direct current. Alternating current, as is associated with electric power system transmission lines, can likewise become stray and use parallel pipelines as a flow path. Alternating current at the usual commercial frequency (60 Hz) does not have as great a corrosive effect per unit amount of current as does direct current. For a given amount of alternating current, the corrosive effect is but a small percentage of the corrosive effect of a like amount of direct current. Nevertheless, with pipelines built on the same right of way and closely parallel to high-voltage alternating-current transmission lines, the amount of alternating current flowing on the parallel pipelines may, under certain conditions, be so great that even a small percentage factor in terms of direct-current equivalents can nevertheless cause serious corrosion attack on the pipeline, and in addition, can constitute a serious personnel hazard (if not properly provided for) because of high pipeline-to-earth potentials often associated with the induced alternating currents.

Within the past few years, there has been the development of the use of high-voltage, direct-current, electric transmission line systems which have been used for the first time in place of high-voltage, alternating-current electric transmission systems. These direct-current transmission lines (known as HVDC systems) involve an additional source of possible stray current corrosion on pipeline systems. Under present concepts, HVDC systems involve transmission of bulk electric power between terminals which may be several hundred miles apart. At each of the terminals there is a high-capacity grounding electrode through which unbalanced system current can flow to or from the earth. Under conditions of unbalance on the HVDC lines, the magnitude of this unbalance current can be quite great, and it will be flowing, as stray current, through the earth along the possibly several-hundred-mile-long path between terminals. The worst condition develops during operation of the HVDC system under emergency conditions with one overhead conductor completely inoperative; full load current then flows through the earth path and through the remaining overhead conductor. Pipeline systems in the vicinity of the terminals will be subject to possible stray current pickup or discharge, depending on the nature of the HVDC transmission line unbalance condition. With improperly designed terminal equipment, or for pipeline systems located too close to HVDC system terminals, pipeline corrosion can be severe. Although the use of HVDC electric transmission systems is presently quite limited, the concept involved is getting greater acceptance with time, and interference from this type of system may ultimately become more prevalent.

Methods of Pipeline Corrosion Control

The material under this heading will be concerned with an outline discussion of the more common means of corrosion-control procedures as they apply to the pipeline industry.

Coatings-The first approach to corrosion control used in the pipeline industry involves the use of coatings. It was early recognized that the corrosion process was of electrochemical origin, and it was quite logically reasoned that if the pipeline metal could be electrically isolated from its environment, there could no longer be a flow of current between separate points on the surface of the pipe and that, as a result, corrosion would be eliminated. This would be perfectly true if an electrically insulating coating could be installed that was 100 percent perfect at the time of installation, and which could be maintained in a 100 percent perfect condition for the life of the pipeline. This is not a practical possibility under the usual pipeline construction conditions. As a result, there will be a certain number of coating defects where the steel will be exposed to the pipeline environment. Although corrosion may be still stopped on better than 99 percent of the pipeline surface, any corrosion current that does flow will be concentrated at coating defects, and the rate of corrosion at these points may be such that pipeline penetration will occur at an earlier date than would have been the case had the pipeline been left bare (assuming coating to be the only corrosion control method used).

Cathodic Protection-Once it was discovered that the use of coatings would not provide the total answer to pipeline corrosion, the technique of cathodic protection was introduced. This is an electrical method of combating corrosion in that any corrosive currents caused by contact between the pipeline and an electrically conductive ionic environment are prevented from discharging from the pipeline to the environment (with attendant corrosion) by nullifying them with a superimposed direct-current flow from an external source. When accomplished, as discussed in Chapter 1, the entire metallic structure being protected is collecting direct current from its environment. By so doing, the entire structure is forced to become a cathode in the electrical circuit (hence, the name of the corrosion control method) and, if the condition is fully satisfied, the corrosion will stop. Although cathodic protection can be applied to bare pipelines, the amount of current required may become so great in the case of large-diameter long pipelines that, in addition to the number and complexity of current sources necessarily installed along the pipeline, there will be a possible problem with stray current from the high-capacity cathodic protection systems causing corrosion on adjacent underground metallic structures of other ownership. As a result of this, time has proven that the best practical combination for use in the pipeline industry under normal conditions is the use of a combination of pipeline coating and supporting cathodic protection. As was indicated earlier, a reasonably well-applied coating can be expected

to protect better than 99 percent of the pipeline surface. With the supporting cathodic protection, current from the cathodic protection system need flow only to the less than 1 percent of the pipeline surface which involves bare pipe metal contacting the adjacent earth. As a result, single cathodic protection installations can, under normal circumstances, protect many miles of big-inch coated pipeline with a minimal amount of current. The combination of the two methods (coatings and cathodic protection) can result in a very high degree of corrosion control on a given section of pipeline.

Stray Current Control-The usual cathodic protection system may not necessarily control high-intensity stray currents from man-made sources of stray direct current. Other methods of control are often required. Since, as discussed, the stray current is simply using the pipeline as a convenient link on which to travel along its path between two points, the major amount of corrosion damage is normally concentrated in the vicinity of the area where the current leaves the pipeline to return to its source (such as the negative bus of a transit-system direct-current substation). Where the distance between the pipeline and the current source is not too great, a common and convenient method of controlling the corrosion is to install a metallic bond between the pipeline and the negative bus of the current source. Current which is removed from a pipeline entirely by way of a metallic path does not corrode the pipeline. Refinements to the simple bond approach may be necessary, particularly in the case of transit systems where there may be more than one direct-current substation involved. This is because, as load conditions vary, a given substation may not continue to collect current through the bond, but at times may tend to permit current to flow from its negative bus, through the bond, back to the pipeline, and hence to another area of discharge where the current can cause corrosion to occur. Under such conditions it is necessary to install blocking devices which will permit the current to flow in one direction only through the bond—and that is toward the negative bus of the current source only. Many refinements of the above basic procedure have been used but it serves to illustrate the basic need.

In the case of HVDC electric transmission systems, discussed earlier, the solution is not as readily arrived at as is the case with the more usual stray current problem. This is because a given HVDC terminal may be either discharging direct current or picking up direct current, depending upon the system unbalance conditions at a given moment. This eliminates the simple bond approach (with or without current blocking devices) which often works effectively in the case of the other types of d-c interfering systems discussed, where the polarity remains constant. By cooperative efforts with the builders of the HVDC systems, installation of HVDC terminal grounds should be located a sufficient distance from the nearest pipeline systems to minimize the amount of stray-current pickup by the

pipelines, assuming that the terminal ground is properly designed. This procedure is practical since the HVDC method is just becoming established, and pipeline system operators are in a position to work with the HVDC system designers to protect their interests. With sufficient separation between the HVDC system terminal and the nearest pipelines, the amount of stray-current pickup can be reduced to the point where it can be overcome by normal cathodic protection systems. Once HVDC terminals are established, no builder of a new segment of pipeline should permit the line to be built so close to an HVDC terminal that a strong stray-current effect exists.

The stray direct-current effects, resulting from disturbances of the earth's magnetic field, are of such an erratic and unpredictable nature that there have not been any hard and fast procedures established for overcoming their effects. Experience has indicated that they are of a transitory nature and that they do not necessarily occur in exactly the same location each time the effect becomes apparent. Because of this, the amount of corrosion damage which can be attributed to the phenomenon does not appear, in most cases, to be established as a significant factor in the overall corrosion-control program.

Internal Corrosion—Although external corrosion is a problem throughout the length of any buried or submerged pipeline, internal corrosion is a problem only if the material being carried by the pipeline is of a corrosive nature. Where the material being carried by a pipeline is determined to be of a corrosive nature, it may be possible to treat the material to inhibit the corrosion properties. Where inhibitors are used, it is necessary to monitor the effectiveness of the corrosion-control method by, for example, use of internal coupons which can be examined at intervals in order to evaluate the effectiveness of the treatment method.

In some instances where treatment is not possible, the use of an internal coating system may be resorted to. In petroleum or petroleum products lines, for example, it is possible to apply paint coatings in place on existing pipelines. Although any paint or coating system applied internally may not be 100 percent effective, it will nevertheless materially reduce the amount of internal pipeline surface which is directly affected by the material being carried. In the case of water pipelines, good experience has been obtained, where internal corrosion is a significant problem, by the use of linings of cement mortar which can be applied to the pipelines in place. In other situations, where conditions warrant it, good experience has been obtained with inserting plastic liners (of a type which are unaffected by the material being carried in the pipeline) inside the original metallic pipe when it approaches the point of becoming unserviceable because of internal corrosion. This approach is normally applicable to lower-pressure pipeline systems only.

Atmospheric Corrosion-Coatings are normally relied on for controlling

corrosion of external pipeline surfaces exposed to either aggressive industrial atmospheres or marine atmospheres. The coatings selected must be suitable for reasonably long-term performance under the environmental conditions of exposure. Even though cathodic protection may be applied to the external surfaces of underground or submerged portions of the same pipeline, this cathodic protection has no effect upon the part of the pipeline exposed to atmosphere because there is no conducting medium surrounding the pipe in atmosphere to conduct protective current to the pipe surface. It is for this reason that coatings only must be relied upon. Coating maintenance must be performed periodically in order to avoid progressive corrosion damage at defects in the coating which will practically always develop during the usual interval between maintenance inspections.

Selection of Materials During Design—In some instances it is possible to eliminate corrosion problems in the design stages of a low-pressure pipeline by eliminating metal as a material of construction. Where conditions are known to be aggressively corrosive to metals, where a substitute material will be adequate from the mechanical standpoint, and where the substitute material will be competitive on an overall cost basis, the use of a nonmetallic material may be a good choice. Materials which are used in the pipelining industry in lieu of metals include, asbestos-cement, reinforced concrete, plastic, and filament wound reinforced plastic pipe which, with development, is finding usage in larger and larger sizes and at higher and higher pressures and temperatures.

Industry Standards and Sources of Information

In the pipeline industry, there are relatively few industry standards which relate directly to corrosion. There are a number of associations and organizations, as given below, through which information on pipeline corrosion may be obtained. Under the following headings are given either the appropriate corrosion standards or the nature of information which can be obtained from the organizations listed.

National Association of Corrosion Engineers

This organization is directly concerned with corrosion of metals in all applications. There is considerable attention given to the pipelining industry in NACE. It is suggested that since standards and guides are published at intervals, getting, from NACE, an up-to-date list of information available is desirable in the event of anyone's wishing to become familiar with information available through NACE at any time following publication of this manual.

Standards—The following standards have been published by NACE. having an application to pipeline corrosion control.

RP-01-69 (Rev. 1)—This is a recommended practice published by NACE and titled "Control of External Corrosion on Underground or Submerged Metallic Piping Systems." This recommended practice addresses itself to recommended methods for pipeline corrosion control as well as criteria and test methods by which the corrosion control system may be evaluated.

RP-05-72—This recommended practice titled, "Design, Installation, Operation and Maintenance of Impressed Current Deep Groundbeds," is related to one type of cathodic protection system ground bed (for use with impressed current systems) which finds its major application on pipelines.

TM-01-72—This test method titled, "Antirust Properties of Petroleum Products Pipeline Cargoes," is concerned with measurement of inhibitor effectiveness in preventing internal surface corrosion in pipelines carrying petroleum products.

Technical Committees—The following technical committees operating within the framework of NACE are organized to direct their attention to corrosion control matters relating to the pipeline industry.

Technical Practices Unit Committee T-3P—Internal Corrosion of Product Pipelines and Tanks.

Technical Practices Committee T-6—Protective Coatings and Linings.

Technical Practices Committee T-10-Underground Corrosion Control.

Publications—The following publications of NACE are directed toward pipeline corrosion control. Following publication of this manual, it is recommended that the reader contact NACE for an up-to-date publication list should he be interested in information of this nature.

Book-Control of Pipeline Corrosion.

American Society for Testing and Materials

Standards available through ASTM currently limited to those standards relating to the testing of pipeline coating materials used for corrosion control. These standards are as follows:

ASTM Designation

Title

G 6-72	Standard Method of Test for Abrasion Resistance of Pipeline Coatings
G 7-69T	Tentative Recommended Practice for Atmospheric Environmental Exposure Testing of Non-Metallia
	Materials
G 8–72	Standard Methods of Test for Cathodic Disbonding of
	Pipeline Coatings
G 9-72	Standard Method of Test for Water Penetration Into
	Pipeline Coatings
G 10-72	Standard Method of Test for Bendability of Pipeline
	Coatings
G 11–72	Standard Method of Test for Effects of Outdoor
	Weathering on Pipeline Coatings

G 12–72	Standard Method for Non-Destructive Measurement of Film Thickness of Pipeline Coatings on Steel
G 13–72	Standard Method of Test for Impact Resistance of Pipeline Coatings (Limestone Drop Test)
G 14–72	Standard Method of Test for Impact Resistance of Pipeline Coatings (Falling Weight Test)
G 17–71T	Tentative Method of Test for Penetration Resistance of Pineline Coatings
G 18–71T	Tentative Methods of Test for Joints, Fittings, and Patches in Coated Pinelines
G 19–71T	Tentative Method of Test for Disbonding Character- istics of Pipeline Coatings by Direct Soil Burial
G 20–71T	Tentative Method of Test for Chemical Resistance of Pipeline Coatings

American Gas Association

AGA does not issue pipeline corrosion control standards as such, but does maintain an active corrosion committee through which information relating to pipeline corrosion control may be obtained. Information may be obtained from AGA by directing inquiries to the association headquarters to the attention of the Corrosion Committee Chairman.

American Society of Mechanical Engineers

ASME publishes the following codes which are, in part, related to corrosion control in the pipeline industry.

ASME CODE

Boiler and Pressure Vessel Code Section VII, Pressure Vessels—Division 1 and 2 Section IX, Welding Qualification

American Petroleum Institute

There are no known codes published by API which are directly related to the control of pipeline corrosion. API may, however, be contacted for information pertaining to pipeline corrosion control in the petroleum industry.

American Water Works Association

The information published by American Water Works Association pertains primarily to the application of coatings used in the water pipeline industry.

National Association of Pipe Coating Applicators

This organization may be contacted for information relative to effective application of pipeline coatings for optimum coating performance on pipelines.

Corrosion Coordinating Committees

Corrosion Coordinating Committees (also sometimes known as electrolysis committees) are regional organizations which have been set up to coordinate corrosion control problems (particularly on pipelines) involving underground metallic structures of different ownership. These organizations normally consider each new installation of cathodic protection or stray current drainage facilities. Information on each case directed to their attention is disseminated to all members of the committee. The cases are considered at periodic meetings of the committee and are closed when all interested parties have indicated their satisfaction with cooperative tests made with the owner of the installation necessitating the test. Should any reader wish to obtain a current listing of active corrosion coordinating committees, this information may be obtained through the National Association of Corrosion Engineers.

Governmental Regulations

Federal Government

There are two sets of minimum federal safety standards applying to the pipeline industry which contain subparts which apply to pipeline corrosion control. Both of these standards are administered by the Office of Pipeline Safety (OPS) of the Department of Transportation (DOT) of the Federal Government. The applicable minimum Federal Safety Standards are as follows:

1. Part 192, Title 49, Transportation, Code of Federal Regulations, "Transportation of Natural and Other Gas by Pipeline: Minimum Federal Safety Standards," that stipulates the minimum requirements relating to the transportation of hazardous gases.

Subpart I is that portion of Part 192 which stipulates the minimum requirements for gas pipeline corrosion control. Part 192 became effective 1 August 1971.

2. Part 195, Title 49, Transportation, Code of Federal Regulations, "Transportation of Liquids by Pipeline." Sections 195.236, 195.238, 195.242, and 195.244 in Subpart D (Construction) pertain to pipeline corrosion control. Sections 195.414, 195.416, and 195.418 in Subpart F (Operation and Maintenance) also pertain to pipeline corrosion control.

State Governments

Any state may issue corrosion control regulations which supplement those pertaining to pipelines as issued by the Federal Government. Any state is free to issue regulations pertaining to pipeline corrosion control which differ from the Federal regulations, provided that they in no way weaken the provisions in the Federal regulations. Should the reader desire information relative to the existence of pipeline corrosion control regulations issued by any particular state, he can obtain that information by addressing his inquiry to the Public Service Commission of the state involved.

Specific Pipeline Corrosion Control Problems

Under the following headings will be discussed some of the problems which face pipeline corrosion engineers in applying satisfactory corrosion control solutions on their systems.

Pipelines in Highly Congested Areas

All new pipelines which are to carry hazardous gases or liquids must be coated and cathodically protected in order to comply with minimum Federal Safety Standards. This applies as well to existing pipelines (except that if existing pipelines are bare, they need not be excavated and coated). Where cathodic protection is to be applied in areas where the pipelines to be protected are closely adjacent to other underground structures, the problem of getting sufficient cathodic protection current to the pipeline in question can become rather acute. Whereas pipelines in open country (particularly if well coated) can be protected with cathodic protection installations at widely spaced intervals along the pipeline, this type of installation is seldom effective in highly congested areas. In these areas, it is usually necessary to install distributed anode systems for either impressed current systems or galvanic anode networks. The distributed anodes need to be placed at frequent intervals along the pipeline being protected through the congested area and so placed that current from any one anode will be able to reach all pipeline surfaces up to the midpoint of the pipe section to the next adjacent anode on either side. Such installations of distributed anodes are complicated as compared to the widely spaced concentrated current source systems (used in open country). These complicated systems involve careful maintenance and careful testing to make certain that current from any anode is not interfering with (and causing possible damage to) metallic structures adjacent to the pipeline being protected.

Protecting bare pipelines in highly congested areas is more difficult than protecting well coated pipelines in the same areas. This is because the bare pipeline requires a far greater amount of current. Compared to the well coated pipe, many high current capacity sources are needed. Additionally, there is a greater possibility of stray current from the anode system interfering with and possibly causing damage to adjacent structures.

The design of a cathodic protection system for pipelines in highly congested areas requires a high level of expertise and should be attempted only by those who are qualified by experience and training in the design of such systems.

Protection of Internal Pipe Surfaces

Where pipelines are required to carry highly aggressive aqueous solutions, some installations may prove to be most economical if steel pipe is used

provided the internal surface can be protected against corrosion as well as the outside. Where the aggressiveness of the material carried is such that coatings alone cannot be relied upon, it may be necessary to design cathodic protection systems for the internal pipe surfaces. A combination of an excellent coating properly applied together with a long life cathodic protection system can make it possible to utilize steel satisfactorily in applications of this nature. It should be noted that even though a pipeline in this service may have cathodic protection applied to its external surfaces, this external protection system has no beneficial effect upon the internal surfaces of the same pipeline. For this reason it becomes necessary to design a completely separate system for the internal surfaces. One solution to the installation of internal cathodic protection in conjunction with coatings is to use strip galvanic anodes of zinc which may be placed on the inside of the pipe along the pipe bottom. Connections between anode and pipe are made at periodic intervals (even as close as each welded pipe joint). To use this type of installation, the current requirement of pipe steel coated with the coating material being used and the particular aqueous environment must be known with a reasonable degree of accuracy. With this information available, it is possible to design installations which will have an expected life of the same order as the expected economic life of the pipeline system on which it is being installed. Zinc is at present the preferred material for use in such installations because it has the highest current efficiency making it possible to design for long life installations. The use of internal galvanic anodes as described is the preferred solution, where it can be shown to be effective, because once installed it requires the least amount of maintenance and is least apt to become ineffective at any time.

Another solution involves the use of impressed current systems. This requires the installation of through-wall impressed current system anodes. These anodes must be electrically insulated from the pipeline steel and must be placed close enough together so that the areas protected by adjacent anodes will overlap each other. Systems of this type are complicated (as compared to galvanic anode systems described above) because of the need for interconnecting cables to feed power from an impressed current power source to each anode. Such installations require a high degree of maintenance in that short circuits developing between anodes and pipe steel can cause the power source to trip off the line. Trouble can also be experienced with interconnecting cables which may corrode through defects in the cable insulation or which may be broken by construction activities on other facilities. The impressed current internal anode system, however, has the advantage of higher levels of current output should it be needed in connection with an internal pipe surface which has a relatively poor coating or no coating at all.

Pipeline Protection in Frozen Earth

With the development of pipeline construction projects in Arctic areas, the problem of providing satisfactory corrosion control for pipelines completely buried in frozen earth (permafrost) has arisen. Evidence indicates that in some types of permafrost soils, corrosion can continue on steel in the permafrost although at a slower rate than would be the case if the pipelines were in the same material unfrozen. The situation is complicated by the probability that any pipeline built in a permafrost region will pass through areas of unfrozen soil inclusions such as at thermokarst lakes and under rivers and streams where the water depth is sufficient to maintain an unfrozen layer beneath the deep ice. Such situations create relatively small anodic areas (at the unfrozen inclusions) which tend to discharge current to large areas of cathodic pipe in frozen earth. This can lead to more rapid corrosion of that portion of the pipeline in the unfrozen inclusion because of the small anode—large cathode effect.

Corrosion control by application of a suitable coating for frozen conditions plus cathodic protection appears to be the desirable protective combination for pipelines in permafrost areas. The coating used must be selected for adequate handling and application characteristics under extreme low temperatures as pipeline construction in certain types of permafrost areas necessitates winter construction in order to permit adequate bearing for construction equipment. The application of cathodic protection poses problems with ground bed anodes for use with impressed current systems for the pipeline in that the anodes may have to be buried in frozen earth. Methods are being developed for coping with this situation. Where impressed current cathodic protection system ground bed anodes can be placed in nonfrozen earth (such as at the bottom of thermokarst lakes), adequate protective current can be discharged from the anodes.

Pipelines which are installed in permafrost areas and which can be allowed to freeze in place can be expected to require substantially less cathodic protection current than would the same pipeline with the same coating in unfrozen earth.

Shorted Casings

Where a pipeline passes through a casing at a road crossing, a railroad crossing, or at other locations where required, good practice calls for having the carrier pipe electrically insulated from the casing pipe. Should a short circuit exist between the pipe and casing in any instance, this condition makes it impossible for externally applied cathodic protection to reach the carrier pipe inside the casing. This is because the shorted casing intercepts the cathodic protection current and carries it to the pipe through the short circuit connection.

Where shorted casings exist, steps should be taken to remove the short

circuit or to otherwise provide for full corrosion control of the carrier pipe inside the casing.

Where the mechanical short circuit cannot be cleared, one procedure is to remove any water from the annular space between pipe and casing and fill this space with an inhibited casing filler such as an inhibited petroleum jelly. This material prevents the entry of soil moisture and debris which might otherwise cause corrosion of the carrier pipe.

A shorted casing which is poorly coated or bare on an otherwise well coated pipeline, creates a load on any cathodic protection system on the pipeline. Since the current required by one bare casing can easily require as much current as many miles of coated pipeline, it is important that where possible the short circuit be removed between casing and pipe rather than using the casing filling technique as described above.

Coating Selection

Matter of coating selection and application is one of the most important matters pertaining to adequate corrosion control systems on pipelines. It is also one of the more abused corrosion control methods. Part of this stems from inadequate selection of the best coating for a particular application and part of it stems from improper application procedures.

There are many coatings available for use on pipelines and it is essential that the coating selected for a particular application be compatible with environmental conditions along the route of the pipeline. Although no attempt will be made here to give any guidance on which coating to select, it should be noted that the best coating for a particular application will be that coating which is most stable throughout its useful life. By stability we mean the obtaining of a reasonably high electrical resistance at time of installation and retaining a high value of insulation throughout the pipeline life with the least practicable reduction in resistance with time.

No matter how carefully a pipeline coating has been selected, it will not perform properly unless it is applied over well-prepared pipe surfaces and in complete accordance with the manufacturer's recommendations. Application procedures for any pipeline project should be complete in all respects regarding pipe cleaning and coating application procedures. These application specifications should be backed up by thorough inspection during the pipeline construction project.

Industrial or Marine Atmospheric Exposure

Where pipelines come above ground in areas where they are subject to a highly corrosive industrial or marine atmospheric environment, the pipeline and its appurtenances may be subject to comparatively rapid corrosion rates from the marine environment. Even though there may be a cathodic protection system on the pipeline, the cathodic protection current will not reach that part of the pipeline in atmosphere. Accordingly, reliance must
be placed upon protective paints or coatings. In less aggressive atmospheric environments, paints may be used for esthetic reasons to give the pipeline and its appurtenances a satisfactory appearance as far as the public is concerned. In the severe atmospheric environments, however, more rugged paints or thick film coatings are required which have been proved to be resistant to the severe environmental conditions. Since there is no cathodic protection back up, any such protective coatings used in these applications must be carefully maintained on a periodic basis.

Controlling and Monitoring Internal Corrosion

Under a prior heading, the use of cathodic protection for internal pipeline surfaces was discussed. In that instance the exposure was to a pipeline full of electrically conducting corrosive material. In other applications, such as in the case of pipelines carrying gas or petroleum or petroleum products, there may be corrosive components transported along with the product which, usually in the presence of condensed water inside the pipeline, can create corrosive elements involved, various means of corrosion control can be used including the elimination of corrosive elements from the product before it enters the pipeline, using various chemical inhibitors to render the corrosive elements ineffective, or taking steps to prevent the condensation of moisture inside the pipeline.

Where there is a possibility that there will be internal corrosion, it is good practice (and required by regulations in many instances) that some type of internal monitoring procedure be used. One common means of doing this involves the use of coupons of the pipeline steel which are inserted in the pipeline at test points so that the coupon material will encounter the product stream and in those zones where corrosion is to be expected. These coupons are removed periodically and inspected for corrosion attack and any corrosion control program adjusted in accord with the results obtained from the inspection program.

In addition to any monitoring program such as that described above, should the pipeline be shutdown and opened for any reason, the internal surfaces of the pipeline should be inspected for corrosion damage.

Electrically Discontinuous Pipelines and Cathodic Protection

The application of cathodic protection to metallic pipelines, particularly existing pipelines, is often compounded by the presence of mechanical joints in the pipeline rather than welded pipeline connections. Mechanical joints, unless provided with a solid bond, can introduce an electrically insulating point at each mechanical connection or, even if not completely insulating, can introduce longitudinal resistance in the pipeline at these mechanical joints. The presence of such insulation or resistance prevents or retards the collection of cathodic protection current and flow of this protection current along the pipeline to a centrally located cathodic protection installation.

Basically there are two alternative approaches to application of cathodic protection to mechanically jointed pipelines. The first procedure involves the uncovering and bonding of each mechanical joint in order that the pipeline to be protected may be made electrically continuous. The problem of locating the underground joints in existing lines and the cost of uncovering and bonding them can be quite expensive, particularly in the case of lines under paving. The other approach is to install separate cathodic protection, usually with galvanic anodes of zinc or magnesium, on each individual section of the pipeline between mechanical joints. Again this involves problems in locating the individual pipeline sections on existing pipelines and involves cost in installing the protection anodes. This method is, however, (depending on individual circumstances) usually the more reliable procedure since failure of any one cathodic protection installation on an individual pipe section will not endanger the cathodic protection on adjacent sections. By contrast, the procedure of bonding pipeline joints and supplying current from centrally located cathodic protection installations can be made ineffective by breakage of any bond cable installed across a mechanical joint because the one breakage will prevent cathodic protection current from reaching all pipeline beyond that break in a direction away from the cathodic protection unit.

Whichever type of procedure is used, periodic inspections must be made to insure that adequate cathodic protection is being maintained.

Needed Standards

Under the following headings are discussed some of the standards which it is felt would be of value for corrosion control programs associated with the pipeline industry.

Standards for Pipeline Electrical Test Points

Pipelines equipped with cathodic protection systems are provided with electrical test points which are installed at intervals along the pipeline to permit periodic test measurement of the level of cathodic protection on the pipeline. At the present time, each individual pipeline company has its own established practices for the construction of such test points. There are differences from company to company as to the number of wires installed at each test point, the manner in which they are terminated, and the color coding of the individual wires. It would appear desirable that the details of test point installation be standardized, particularly insofar as color coding is concerned, so that when cooperative tests are made between pipeline systems, there will be no confusion as to the meaning of the color coding which will then automatically indicate the nature of the test point. As further justification, there are usually several types of test points used along a pipeline. These may, among others, include test points at cased crossings with wires to both casing and carrier pipe, normal potential test points along the route of the line with wires directly to the pipeline for potential measurement purposes, and test points with wires bridging calibrated pipe spans so that the current flowing in the pipeline can be measured. If the test point construction and color coding are standardized, there would then be less possibility or confusion as to the type of test point being worked with at any given location.

Standards for Monitoring Internal Corrosion

Minimum Federal standards for corrosion control on pipeline carrying hazardous gases or liquids require that there be some form of monitoring for internal corrosion in the case of products containing corrosive elements. The standards further provide that the internal monitoring provisions shall be inspected at periodic intervals. The exact nature of the monitoring devices is not set forth.

It would appear to be timely for the establishing of standards for monitoring internal corrosion on pipelines. These standards could be established for various classes of service and could set forth accepted monitoring devices or procedures applicable to these classes of service. It should be noted that earlier reference has been made to NACE standard on internal corrosion monitoring on petroleum products pipelines.

Standards for Pipeline External Corrosion Surveys

The minimum Federal standards for corrosion control on hazardous gas and liquid pipelines provide that, where possible, electrical surveys be conducted on pipeline systems to determine the status of corrosion control. There are no provisions in the standards setting forth the details for such electrical inspection. At the present time, various companies seeking to comply with the minimum federal regulations are conducting pipeline corrosion surveys with various requirements as to frequency of inspection along the pipeline route and the manner in which the inspections are to be made.

It would appear that it is timely for the establishment of standards for pipeline corrosion surveys which will be used in complying with minimum federal pipeline safety standards.

Summary

The pipeline industry is a very high investment industry. Fully implemented corrosion control can effect high dollar savings by reducing property loss, by reducing the cost of repairs, by avoiding catastrophic failures with loss of property and life, and by conservation of natural resources as the energy shortage crisis becomes ever more serious.

There are effective methods of corrosion control which are available for

both the external surfaces of a pipeline and for its internal surfaces where they are required. At the present time, specific standards concerned with corrosion and directly related to the pipeline industry are minimal. Governmental regulations are now in effect relative to pipeline corrosion control requirements for major segments of the pipeline industry. These regulations will encourage the development of additional standards directly related to pipeline corrosion control.

There are a number of associations through which information related to pipeline corrosion control may be obtained as stated herein.

Chapter 6

Corrosion Standards and Control in the Telephone Industry

George Schick¹

The discussion of corrosion and corrosion protection in the telephone industry requires the division of the telephone plant into two major areas: outside plant and central office equipment. The outside plant, which includes all the cables, closures, hardware, radio towers, etc., requires relatively advanced corrosive degradation before it stops functioning properly. It is also the part of the plant which is the most exposed to the corrosive environment. Central office equipment on the other hand is always located in a building and exposed to a relatively controlled environment. However, technological advances have resulted in the development of sophisticated components, usually small in size, and this has led to closer component spacings, with separable electrical contacts having lower contact forces and voltages than previously possible. In this type of equipment even microgram quantities of corrosion products can result in premature failure.

In view of these basic differences the corrosion problems and their solutions are quite different. The amount of capital investment and cost of repair or replacement, due to corrosion failure, is, by far, larger for the outside plant than for the central office equipment. The major part of this chapter will therefore discuss outside plant corrosion problems and means of their protection.

Outside Plant

The outside plant is that part of the telephone plant which is located between the subscriber's side of the main distribution frame in the central office and the protector block on the subscriber's house. From the corrosion standpoint the outside plant is subdivided into the following areas: (1) aerial plant; (2) underground plant; (3) buried plant; and (4) submarine cable systems.

The aerial plant is subjected to the corrosive effects of rain and dew. The

¹ Bell Telephone Laboratories, Whippany, N.J. 07981.

areas considered to be the most corrosive are the sea coasts where the wind blows salt-laden water, and the industrial areas where the air is polluted by acidic fumes.

The underground plants are characterized by cables enclosed in conduits and joined in manholes. Although the conduits provide substantial mechanical protection, they are not impervious to moisture and are often flooded by soil waters. The manholes in many locations are partially or completely flooded and polluted manhole water has a strongly corrosive effect on cables and associated equipment. It is also possible that cables in flooded ducts or manholes pick-up or discharge stray d-c currents.

The buried plant is characterized by cables and splice closures directly buried in the ground with access points brought above ground in pedestal type terminals. This plant is exposed to both corrosion and physical and biological degradation. Physical damages are inflicted by rock cuts or lightning, biological degradation is caused by rodents and ants, and corrosion is caused by soil waters which can be as acidic as pH 3 and as alkaline at pH 10. Stray currents are also playing an important role in the corrosion of buried plant.

Ocean cables and their accessories are exposed to one of the most corrosive natural environments, the sea. In this environment the situation can be further aggravated by the abrasive effect of coral and physical damage caused by trawlers.

The protection against all these hazards is partially built into the components of the plant and partially applied to the working plant. The built-in protection is primarily based on the choice of materials.

Materials in the Outside Plant

Since about one third of all telephone plant investment is in cables, the materials in cables and cable sheaths will be discussed first. The corrosion protection of the cables is largely built into the cable sheaths. Therefore, materials in the various sheath constructions will be emphasized.

Basically all cable designs are either multipair or coaxial. The former is characterized by bundles of conductor pairs where the individual conductors are surrounded by a dielectric material. Coaxial cable is made with a single center conductor surrounded by a coaxial conductor tube (outer conductor) and separated by polyethylene disks or solid polyethylene dielectric (ocean cable).

The amount of built-in protection depends upon the channel carrying capacity and future accessibility of the cable. Toll cables, which have large channel carrying capacity over long distances, have more built-in protection than smaller distribution cables. Distribution cables in turn have more built-in protection than service wires and drop wires.

Multipair Cables and Cable Sheaths

The conductor material is either copper, tin-plated copper, or aluminum. Insulation for the copper conductors is provided by paper pulp, paper ribbon, low density polyethylene, or propylene copolymers. The latter two are designated as PIC insulation. The aluminum conductors are insulated with low density polyethylene or propylene copolymers.

Protection of the cable core against water ingress is achieved by dry air pressurization (pulp cables) or by filling the core with polyethylenepetroleum jelly mixtures (PIC cables).

Core or unit binders are used to hold together either the entire core or part of the core (usually 25-pair units). The material of these binders is either polypropylene copolymers or high density polyethylene.

Core wrap holds together the core in its assembled condition and size, adds to the dielectric strength between the conductors and the shield and protects the core from heat damage. In PIC cables the core wrap is made of either polyethylene terephthalate (mylar), polypropylene or styrenebutadiene rubber tape. The core wrap for pulp cables is paper.

The cable sheath protects the core from the environment mechanically, electrically, and chemically. The sheath must perform effectively for 40 years or more and for those occasions when it fails, should be readily repairable.

The standard sheath for telephone cables until the late 1940s was lead. After the Second World War, this metal became scarce and expensive, triggering the development of composite sheaths. Small quantities of lead sheathed multipair cables are still produced for special installations, for example, over steam locomotive tracks and where gasoline contamination is anticipated.

The composite cable sheath may have some or all of the following components; starting from the core wrap and progressing to the outer surface.

1. Adhesive coated aluminum—serves as diffusion barrier. The aluminum is EC grade and bonded with ethylene acrylic acid copolymer to the inner jacket.

2. Inner jacket—provides liquid water block and isolates the core from high potentials on the shield. The inner jacket is made of high density polyethylene.

3. Shield—provides electrical shielding and interception of lightning and power-cross currents. The shield is made of EC aluminum, plastic-coated EC aluminum, or copper.

4. Soldered steel shield—provides hermetic seal (for pulp cable), low frequency electrical shielding, and armoring against rodents. This shield is protected against corrosion with a bituminous thermoplastic flooding compound. The shield material is mild steel or tin-coated steel. In some

cables where hermetic seal is not needed but corrosion and rodent resistance is essential the electric shielding and steel shield are combined in bimetallic shields which can be copper and stainless steel or plastic-coated aluminum and stainless steel.

5. Outer jacket—provides mechanical and environmental protection for the underlying members. This jacket is made of low density polyethylene.

Multipair cables intended for use inside buildings (still part of the outside plant) need fireproof insulation and polyethylene is unsuitable for this purpose. In these cables the conductors are dual insulated with low density polyethylene and polyvinylchloride. The core wrap is mylar (polyethylene terephtalate) and the aluminum shield is coated with vinyl chloride-vinyl acetate-maleic acid terpolymer and bonded to a polyvinylchloride jacket.

Outside Plant Wires and Cables

The outside plant wires are used in the aerial, and buried plants.

Drop wire is used in the aerial plant between the junction with an aerial distribution cable and the customer's residence. The conductors are made of copper-plated steel. The conductors are insulated with vulcanized styrenebutadiene rubber. The insulation is reinforced with rayon servings and the outer jacket is made of vulcanized polychloroprene (neoprene).

Service wire is used in the buried plant between the junction with a buried distribution cable and the customer's residence. The conductors are copper-coated steel insulated with high density polyethylene. The insulated conductors are surrounded by a polyvinylchloride inner sheath. Electrical shielding is provided by aluminum tape and the outer jacket is polyvinylchloride.

Underground wire is used in the rural buried distribution plant between junction with aerial or buried distribution cable and service wires or the customer's residence. The conductors are made of copper insulated with low density polyethylene. The conductors are protected against rodents with galvanized steel tape and the outer jacket is polyvinylchloride.

Coaxial Cables are used as long haul toll cables. The center conductor is copper, separated from the outer coaxial tube by slit disk, high density polyethylene dielectric. The outer coaxial tube is both electric conductor and strength member and made of copper tape and tin-plated steel, laminated together with ethylene-acrylic acid copolymer. The coaxial units are insulated with paper and surrounded by an inner low density polyethylene sheath for dielectric strength. The polyethylene is covered with a paper heat barrier on which the lead electric shield is extruded. The outer corrosion protection is provided by a bituminous coating and a low density polyethylene outer jacket. Since these long haul toll cables require a high degree of reliability, pulp insulated copper conductor pairs are distributed along the coaxial units to serve as water alarm circuits.

Armorless ocean cables are used in the deep ocean where protection

against trawlers is not necessary. In this cable the strength member is a high strength steel strand located in the center. The inner conductor is a copper jacket surrounding the steel strand. The dielectric separating the inner conductor and the concentric copper tape outer conductor is medium density polyethylene. The outer protective jacket is high density polyethylene.

Ocean cables laid on the continental shelf need more mechanical protection. This is achieved with helically applied galvanized high-strength steel armor wires which are either coated with bituminous flooding compound and jute or individually jacketed with neoprene.

Outside Plant Apparatus

The outside plant apparatus items are so numerous that their complete description is clearly beyond the scope of this book. We are therefore restricting ourselves to the discussion of the materials of some of the most basic items.

Splice closures are the points where the cables are joined together. Because the joints must have a high degree of electrical contact reliability, these closures must be resistant to the corrosive environment.

Underground and buried plant uses hot dip galvanized cast iron splice closures for multipair cables. The closure halves are tightened together with type 304 stainless steel bolts and nuts. The inner cable clamp is also type 304 stainless steel. The end plates, through which the cable enters into the splice closures are made of a lead-bismuth alloy. Moisture-proofing of the joined half closures is assured by a butyl rubber tape. Splice closures in the buried plant are further protected with a bituminous mastic primer and a hot applied tape (cotton fabric base saturated and coated on both sides with a bituminous mastic). The splice closure for coaxial cables is tin-plated steel tube with wiped-on lead alloy end plates. The outer corrosion protection is the same as that of the galvanized cast iron buried splice closures.

Splice closures and repeater houses for ocean cables are made of copperberyllium alloy since the environment is very corrosive and the system once in place is virtually inaccessible.

Aerial plant uses mainly plastic splice closures in the distribution plant which offers little corrosion protection since ready accessibility is its most important feature. In such closures the joining elements are either made of brass or the joint has its built-in encapsulant. Splice closures providing corrosion protection in the aerial plants are made of cast aluminum.

Loading coil cases have two main types. The cover is either bituminous hot melt coated steel or low density polyethylene. The latter contains polyurethane inner space filler and a steel coil container. The loading coils are made of permalloy or magnet wire (thermoplastic or thermosetting coating on copper conductors). The steel covered type has nylon coil spacers and the coil encapsulant is silica powder-filled epoxy. The encapsulant in the polyethylene cover type loading coil case is polyurethane.

Protected terminal blocks are sometimes used in ready access terminals of multipair cables. The shell of these terminals is made of 50 percent acrylonitrile/butadiene styrene (ABS) and 50 percent polyvinylchloride blend. The pigtail conductors (tinned copper) are insulated with polyvinyl chloride, and the encapsulant used is foamed polyurethane.

Coaxial terminals in the underground plant are red brass shells (85% Cu + 15% Zn) with electroplated tin coating.

Hardware

In the aerial plant the telephone plant is located on telephone poles. With the exception of the self-supporting cables, which have their own built-in strand, all cables are attached to strands. The cables are secured to the strand with lashing wires. At the wooden telephone poles, clamps, hooks and fasteners are used to secure the strands, cables, closures, etc. to the poles. The poles themselves may contain pole steps and are secured against high winds with guys and anchors. With the exception of 400 series stainless steel strands and lashing wires, used in corrosive areas, practically all hardware items are made of galvanized steel. In some areas aluminum coated steel hardwares are also used.

In the underground plant a large number of hardware items are used in the manholes (racks, hooks, ladders, manhole steps, etc.). In the majority of the manholes these items are made of galvanized steel. In particularly corrosive areas where the manholes are flooded, the racks, hooks and their fasteners are made of Monel.

Outside Plant Corrosion Standards

The materials described in the previous section provide substantial protection against corrosion. In fact, they are the only protective measures in the aerial plant, but they do not solve all the corrosion problems encountered in the underground and buried plants. Bare metallic structures, such as lead cable sheath, splice closures, and hardware are exposed to corrosive soils or high water tables. The non-metallic protective coverings are subject to physical damages, degradation by aging and lightning and the underlying metallic layers are partially exposed to the corrosive media. The underground and buried plants, besides the natural corrosion by interaction with the environment, also are subjected to stray current corrosion.

This section will discuss corrosion, corrosion surveys and corrosion mitigation of underground and buried telephone plants both in non-stray and stray current areas.

General Principles

The telephone plant corrodes where current leaves the sheath and flows into the electrolyte (earth). Any current which leaves the outer metal

surfaces (primarily lead cable sheath) must have entered it at some other point. (To simplify the following description, the term "cable sheath" or "sheath" will also mean splice closures and associated hardware.) The general attack on the buried and underground telephone plant corrosion problem, therefore, consists of two equally important phases:

(a) Limiting as far as practicable the current which enters the cable sheaths.

(b) Providing metallic paths through which the current may leave the cable sheath without damaging it or other foreign buried metallic structures.

The range of conditions encountered in corrosion problems are extremely wide. The currents involved may be manmade, otherwise called stray currents: (1) dc transportation systems, including mining operations; (2) dc power and lighting circuits; (3) d-c welding processes; and (4) cathodic protection rectifiers on cables, pipe lines, ships in dock, steel piers, metal framework of buildings, storage tanks either buried or above ground, and gas, oil and water wells.

Currents may be caused by natural conditions (non-stray currents): (1) dissimilar metal couples; (2) differences in the composition of metals exposed to the electrolyte; (3) variations in earth resistivity; (4) variations in soil composition; (5) differential aeration; and (6) sulfate reducing bacteria.

The distance between the locations where the current is entering the sheath and where it is leaving may range from minute fractions of an inch to miles. The former are called local cells, the latter are long cells.

The determination of whether or not corrosion is occurring requires careful measurements and the data obtained must be subjected to careful analysis.

Protective arrangements should be such as to minimize the probability of impressing current on plants owned by others. Since protective schemes against corrosion mutally interact with other structures, cooperation through local corrosion committees is a must.

Limitation of Current Pick-up

Two things must be done if the flow of current to the cable sheath is to be at a minimum:

1. Except for interconnections which are specifically planned as part of a coordinated protection scheme, the underground and buried plant should be kept free from all connections to other grounded metallic structures.

2. The cable sheath should not be made more negative to earth in any area than is necessary from the practical design standpoint.

Negative cable-to-earth voltages can be kept low by increasing the number of drainage points and decreasing the current drained at each point. Even with a carefully designed drainage system, there may be a tendency toward high negative protentials in a few areas.

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General Principles of Drainage

Current enters the cable sheath because a potential difference is impressed by an external source or by self-generated electromotive forces. All currents entering the sheath must leave it. The sheath can be prevented from corroding by permitting the current to leave through a wire rather than by leaking into the electrolyte.

If a drainage system is to approach the objective of providing protection with minimum negative-to-earth voltage, minimum current flow on sheaths, minimum reaction on plant owned by others, etc., it must be based on a study of the driving potentials and currents in absence of drainage. In a well-adjusted drainage system, the currents are permitted to follow the paths indicated by the driving potentials as far as practicable, the major difference between "drained" and "undrained" conditions being that currents leave the sheath via a metallic connection rather than by leaking from the sheath directly into the electrolyte. The drainage process must change the cable potentials and hence the current distribution and direction of flow somewhat, but these changes should be as few and as small as practicable.

Where sheath currents are due to stray currents, it is usually practicable to complete the circuit for the currents by means of wires between cables and the source of the stray current.

In non-stray areas the current must be taken off the cable through a wire and put into the earth through expendable anodes. In many cases a source of d-c power must be used, in others the natural galvanic potentials between the cable sheath material and certain anode materials, such as magnesium, can be used in this process (cathodic protection). The anode locations should be chosen so as to minimize the current to other metallic structures.

Tests

The objective of corrosion tests is to find out where and why current is entering the sheath and in what amounts, where it is trying to go, and where and how one can let it go there without causing corrosion. The testing techniques are numerous, but whatever the test, its ultimate objective is to tell something about current. Since there are no direct methods to measure the currents being picked up or discharged in a short cable sheath section, it is necessary to resort to various forms of indirect measurements. Cable-to-earth voltages can indicate whether currents are picked up or discharged but they do not indicate the rate of pick-up or discharge and they do not always indicate whether the cable is picking up or discharging current. An adequate corrosion investigation, therefore, uses many kinds of tests.

Once an adequate protective system is established it is important to watch its performance to see that it remains adequate. This is done in two general ways. (a) Periodic "routine" surveys.

(b) Use of "pilot" wires to central testing points so that checks can be made at short intervals of conditions at "key" points.

Routine surveys are time consuming and expensive and usually made not more than once a year. "Key" points with "pilot" wires can be checked very frequently with a minimum of time and expense.

Stray Current Corrosion and Corrosion Protection

Voltage differences exist between different points on the running rails of the d-c transportation systems due to IR drops in the rails caused by the current discharged to the rails through railway propulsion motors, car heaters, etc.

The earth, in which cable and piping systems are imbedded, forms a path parallel to the rails. Part of the current delivered to the rails flows through the paralleling earth path between points of higher and lower rail potentials. In turn, part of the current in the earth flows between these areas over cable and pipe systems. The higher the longitudinal resistance of the rails and the lower the leakage resistance of the rails to earth, the larger will be the proportion of the rail current which flows in the earth. The proportion of the earth current carried by cable and piping systems is a direct function of their leakance to earth and an inverse function of their longitudinal resistance.

Measurements of Rail Voltages

In many cases adequate drainage systems can be designed without knowing quantitatively the rail potential distributions. However, in some cases quantitative information is desirable, that is, for explaining observed cable-to-earth and cable-to-rail voltages, in studies to select the best drainage points. Such measurements are: (a) direct measurements of rail potentials using pilot wires and (b) measurements of rail gradients in the field.

In the pilot wire scheme cable pairs are used to connect selected points on the rails to a central testing location. Measurements from each of these points to a single point (namely, rails at the substation) or between different points can then be made using recording or indicating meters. This method is used only where information extending over a considerable period of time is desired. Some long pilot wires will have high resistance and to avoid corrections high resistance meters are required. If a particular pilot wire is common to two or more meter connections, the current taken by some of the meters will react on the readings of the others because of the drop over the common resistance. This effect can be avoided by high resistance meters and low resistance pilot wires. If sufficiently low resistance cannot be obtained the mutual effect can be excluded by using separate pilot wires for all simultaneously connected meters.

General Principles in Design of Drainage System

There are many places in a rail system where the voltage gradients change sharply. In some cases they change in such a way as to provide points where the rails tend to pick-up current and undrained cables tend to discharge current to earth.

An idealized approach is to eliminate all existing drainage and a careful survey made to define areas in which the cables are picking up or discharging current, where the cables become positive to rail and what are the rail potential differences, sheath current magnitudes and directions. At key points the measurements should be made with recording instruments for 24 h and weekends. Based on the pictures thus obtained a drainage system has to be designed to establish protective cable-to-earth potentials with minimum current pick-up by the cables. This can be accomplished by first installing drainage connections to rails as far away from the substation as any significant positive cable-to-rail voltages are observed. Most of these connections would require automatic reverse current switches. Next, additional drainage connections have to be installed closer in toward the substation as needed to keep the cables from discharging current to earth at any point. Automatic reverse current switches and current limiting resistors should be installed in these drainage connections as needed. Drainage connections normally should be made to rails rather than substation buses in order to secure the best coordination between drainage current and protection.

In the practical case it frequently is not possible to remove all drainage from an urban cable plant while a complete survey and analysis are being made. However, by analyzing the rail potential pattern and the cable layout it is usually practicable to find the points where outlying drainage connections might be made in the absence of existing drainage. Tests can then be made at such locations with the existing drainage connections open for a few minutes at a time. Any such outlying drainage connections found to be practicable then can be installed and the drainage connections nearer the substation rearranged if necessary.

Determining Whether Protection is Being Secured

In large parts of stray current areas voltage measurements between cable sheaths and earth (usually in bottoms of manholes) are sufficient to indicate whether current is being picked up or discharged; negative cable-to-earth voltages indicating pick-up areas and positive voltages indicating discharge areas. In some new steel reinforced concrete manholes the voltage is measured 75 to 100 ft away from the manhole in either direction along the cable route. Such indications are usually reliable where the voltages are larger than those observed because of galvanic potentials (over 0.1 V). The rate of current pick-up or discharge is not indicated by the voltages since it also depends on the leakage resistance of the cables to earth. Generally where the leakage resistance is low the cable-to-earth voltage is usually lower and more steady than in adjoining areas. Hence, readings of this type are likely to indicate danger areas or contacts between cables and other grounded structures. Cable-to-earth voltages can thus be used to block out the major pick-up and discharge areas.

In some areas of uncertainty sheath current measurements or measurements used in nonstray current areas are used. In a small residue even these measurements may not be completely indicative and probably the best way to dispose of those areas is to increase slightly the drainage currents at nearby points.

Protection Against Cathodic Corrosion

Under some conditions cathodic corrosion of sheaths may occur where the cable-to-earth potential is over a few tenths of a volt negative. In the presence of salts this critical voltage may be as low as 0.2 V. Methods of preventing cathodic corrosion are:

1. Keeping the negative cable-to-earth potentials as low as practicable.

2. Judicious use of insulating joints shunted, if necessary, by resistors and/or capacitors.

3. Replacement of cables, failed by cathodic corrosion, with polyethylene jacketed cables.

4. Periodic flushing of ducts to remove accumulated alkali.

Competing Drainage Systems

In many areas water or other piping systems are also drained. If the potential of a piping system, having low leakage resistance to earth, is reduced by drainage the earth potential in its vicinity tends to be reduced. As a result, the tendency for current to be discharged from a nearby telephone cable is increased. This may increase the difficulty of providing adequate protection to the telephone plant particularly if the pipes are drained directly to the negative bus at substations. However, by virtue of the high leakage of pipes to earth the adverse effect of pipe drainage usually does not extend over long distances except where the pipes are of unusually low longitudinal resistance. If pipe drainage makes it difficult to provide protection to the telephone cables, a coordinated drainage system, through cooperation with other parties concerned, is the solution.

Surveys and Test Methods

Routine surveys involve a set of measurements made periodically to check the corrosion conditions of the telephone cable plant. These surveys determine: (a) areas where cable sheath is liable to damage from corrosion; (b) important differences from any previous survey; and (c) what further data may be required for determining necessary measures of protection. The periodic measurements include: (a) potentials of cable sheath to ground, nearby rails, and pipes; (b) current in cable sheath; measurements made at approximately the same time as potential measurements; and (c) overall check tests made at more frequent intervals than the above potential and current measurements.

A check of any drainage wire fuses and automatic switches should be made as a preliminary part of the routine surveys to avoid wrong conclusions. Underground dips in the aerial plant should be included in the routine survey.

In general routine surveys should be made yearly, however, the frequency of the survey is influenced by local conditions to maintain satisfactory plant operation. Where routine surveys are made less frequently, overall checks are needed at approximate intervals. In the sections of the country where the ground is frozen to appreciable depth, surveys during the winter months should be avoided. In other sections, dry and wet seasons should be taken into account.

Measurements of Cable Sheath Potential

Cable sheath to earth potentials are measured initially to have a qualitative indication where the current is collected and where it is discharged. Supplemental measurements are made of the cable voltage to adjacent rails, water, and gas pipes or other extensively grounded metallic structures. When manholes are opened for routine survey measurements, these should include measurements of cable sheath to electrified railway rail where the rail runs closer than about five feet; when greater than five feet but on the same street from every second or third manhole. Measurements to pipes via house connection, hydrants, or gate boxes should usually be made at every second or third manhole and also at points where the main pipe lines themselves are accessible.

Since the potential will fluctuate in many cases, the voltmeter scale should be observed a sufficient amount of time to obtain reliable average value. In congested areas, readings should be taken every 30 s for 5 min, taking the average positive indication and the average negative indication. At manholes where sheath currents are also measured, these should be correlated with the potential measurements. In less congested areas the readings can be taken in 3 to 5 min intervals for half an hour or more. In cases where there are both positive and negative potentials, an estimate should be made of the percentage of time during which the cable is positive.

Under normal circumstances the potential of the cable to earth is best represented by contact with damp earth about five feet distant from the cable run. A copper/copper sulfate half cell or lead tipped rod or lead ground plate should be employed for earth contact.

Current Measurements on Cable Sheaths

In routine surveys, data on amount and direction of sheath current are obtained by potential drop measurements over a measured length of cable sheath. A millivolt scale is used for this purpose. These current measurements supplement the potential measurements to determine their significance. A comparison of results along the cable run will give an approximate indication of the areas where current is collected and where it is discharged.

It is desirable to make current measurements at or adjacent to each point of change in conductivity or junction of cable routes including short spurs or laterals. Between such points it will be desirable to make current measurements at about half the manholes where potential measurements are made or more often if consistent increases or decreases of current are noted.

For any particular manhole, current measurements should be made at the same time as the voltage measurements. The current corresponding to the millivolt drop is computed from the sheath geometry and conductivity. Careful note should be made of the direction as well as the amount of current. As in the case of voltage measurements, observations should cover a sufficient period of time to give reliable average indication depending on the car or train headway.

Current measurement in drainage wires is made in a number of ways: (a) insertion of an ammeter in series at the fuse terminals; (b) drop of potential measurements over a section of the drainage wire; and (c) drop of potential measurements from a "Central Testing Bureau" over a section of the drainage wire.

The overall checks should include current measurements on jointly used drainage wires. Tie bonds between cable sheaths of the telephone company and other subsurface structures should be checked in the same manner as other drainage wires about once a year.

Visual Inspection

In connection with routine surveys, notes should be made of the following conditions.

(a) Evidence of corrosion.

(b) Any unsatisfactory conditions of cable bonding or racking in manholes.

(c) Cables submerged in flooded manholes.

(d) Water running through ducts containing cables.

(e) Accidental or unauthorized contacts with pipes or other metallic subsurface structures.

(f) Evidence of unusual amount of ground water in the vicinity of the duct line; for instance, springs or marshy ground.

(g) Evidence of cinder fills.

Duct Surveys

In some locations electrolysis measurements made at manholes do not indicate the probability of corrosion of cable sheath in the ducts. This may occur at stray current areas where the cable is very locally affected by another underground structure crossing the duct line. It can also occur at nonstray current areas where the potentials between cable and earth are small, and relatively small variations may be important.

A duct survey consists of moving a lead slug through a spare duct and measuring the cable to slug potential, the slug leakage current, and the slug leakage resistance at regular intervals throughout the duct length. Since the duct survey is more costly than manhole measurements it is warranted only at the following locations: (a) where failures have occurred but where the manhole measurements did not justify remedial measures; (b) where corrosion is suspected or has been observed; and (c) where positive potentials have consistently been found in the manhole measurements made in past routine surveys.

Duct surveys can be made only in nonmetallic ducts. They are particularly well adapted to tile conduits.

A duct slug consists of a piece of 2-in. diameter lead cable sleeving cut to about a 14-in. length. A 6-ft piece of 18-gage stranded wire with tough rubber insulation is soldered to the inside of the sleeve at least 1 in. from the end. The sleeve is then placed over a wooden duct rod so that the wire will trail the slug when inserted in a duct, and the front end of the sleeve is beaten down around the rod about 6 in. from the end. The sleeve is then filled to about 1 in. from the open end with No. 1 pressure plug asphalt. A protective band of lead is placed around the rod and wire and the open end is beaten down around this band.

Where there are several ducts available, a low duct should be used because there is more chance to encounter silt, mud, or moisture. In some instances upper ducts may be selected because a failure occurred or a cable will soon be placed in it.

Of the three measurements to be made at any location the *cable-to-slug* potential must be made first to avoid polarization from the other measurements. The same considerations apply to this measurement as to the *cable-to-earth* potentials at the manholes. However, because the resistance to earth of the slug is likely to be high compared to that of a manhole ground plate the use of a high sensitivity (200 000 ohms/V) center zero voltmeter is advisable. With such an instrument, no correction for the resistance of the slug is necessary. Where a relatively low sensitivity voltmeter is used, the readings should be corrected wherever the slug resistance exceeds about 10 percent of the meter resistance. The corrected potential (E_e) is computed by

$$E_c = E_m \left(1 + \frac{R_s}{R_m} \right) \tag{1}$$

where E_m = measured potential

- R_m = resistance of the meter on the scale used
- R_s = resistance to earth of the slug

Slug leakage current is measured by connecting a low resistance milliammeter between the cable and slug, in place of the voltmeter. This direct measurement also takes into account the polarization of the slug which may result from the leakage. This polarization may cause a drop of the current value and the reading should be taken after 30 s to 1 min when the needle becomes steady. The resistance of the meter should not be more than 0.5 to 1.5 ohms. This can be achieved by using shunts on low resistance meters.

Because cable to earth resistance is small, the measurement of resistance between the duct slug and the cables is very nearly the same as the duct slug leakage resistance. Duct slug resistance can be measured by either a d-c or a-c method. The d-c method may used 1.5-V external potential between the cable and slug and measure the current. Direct readings can be made with a volt-ohmmeter. Since an externally applied current rapidly polarizes the slug, the maximum swing of the needle should be read. To eliminate the effect of normal cable-to-slug potentials, two readings must be taken with reversed polarities and the average used as the resistance value. To limit the polarization effect, the external potential should be applied only long enough to make the readings.

An a-c method or a method employing rapidly reversing dc is prefered to the d-c method to exclude the polarization effect. An instrument called Vibroground uses a vibrator for reversing the current and the reading is obtained by adjusting a dial to get zero deflection on a meter. A few 1000-ohm scale on the instrument is necessary for duct surveys. Other instruments are Direct-R Ground Tester and Megger types.

In some cases duct surveys may be used to determine the effect of drainage. In this case two surveys are required, one with the drainage disconnected and one with the drainage operating. The drainage should be disconnected several days before testing with drainage off.

In the interpretation of the measurements the duct slug can be considered as representing a small piece of the working cable sheath. In general the same interpretation applies to the cable-to-slug potential as the cable-to-earth potentials at the manholes. The measured potential may be in error as much as 0.1 V due to the difference in the electrode potentials of cable sheath (covered with corrosion products film) and the duct slug (scraped to bare metal at least partially). This is an important consideration at non-stray current areas. True cable conditions are more closely indicated if a slug is left in the conduit undisturbed and bonded to the cable for two to six months and readings taken after removing the bonds on the stabilized undisturbed slug. Cable-to-slug potential may be subject to fluctuations due to the operation of grounded d-c systems some distance away from the test location. Under such conditions it may be desirable to take a 24-h record of the potential with the slug at a critical point in the duct.

Positive cable-to-slug potential indicates the tendency for the cable to corrode and negative potential indicates non-corroding cable. Where the cable-to-earth resistance is high, very little corrosion may occur with positive cable potentials of appreciable magnitude. Sudden changes in potential, particularly isolated high readings, may indicate the presence of foreign material, such as steel wire, in the duct. Such readings have little significance from the corrosion standpoint.

Experience shows that leakage current from the slug in excess of 2 mA indicate a need for corrosion protection and leakage current below 0.5 mA does not warrant remedial measures. Current values between these two need other considerations, such as the number and importance of the cables, and the cost and maintenance of protective measures. Higher leakage current can be tolerated from a completely submerged slug than from a slug with limited area of contact with the electrolyte.

Duct slug resistance is affected by the moisture or liquid in the duct and is frequently lower in the low duct than in the high duct. Rainfall or dry weather may cause changes. It is, therefore, important to consider the condition of the duct for the interpretation of the resistance readings. The measurement of duct slug leakage resistance not only permits correction of the potential and current readings, but also indicates the possibility of corrosion, since points of low resistance to earth are more likely to be corroded than points of high resistance.

Test Methods in Non-Stray Current Areas

Earth Gradient Measurements

Figure 1 shows a cross section of a cable lying in the earth. It is assumed that the cable is discharging current radially into the earth. IR drop measurements, through the earth between a point on the surface of the earth directly over the cable A and points on each side of the cable B and C can determine whether the earth near the cable is at a higher or lower potential, than more remote earth. If point A is at higher potential than B and C, current is flowing away from the cable. Measurements on each side of the cable are made to establish whether or not there is a "transverse" current in the earth, which produces IR drop across the surface of the earth but does not involve the cable. Such current would be indicated if, for example, point A were at a higher potential than B and lower than C. When an indication of transverse current is obtained the determination of whether the cable is picking up or discharging current is difficult.

Earth gradient measurements are made with electrodes whose potential is not affected by the environment. As the ordinary lead plate is variable in this respect, the best choice for measurements in the field is the copper/ copper-sulfate half cell. The contact resistance between this half-cell and



FIG. 1—Cross section of cable discharging current into the earth.

the earth may be quite high, therefore, a meter having high resistance (200 000 ohms/V) should be used.

The direction of current flow due to earth gradient can be determined with three half cells in which case, prior to the measurements, the half cells have to be calibrated on a glass tray containing a conductive solution, and the differences used as correction factors. Another method using only one half cell, illustrated in Fig. 2, does not necessitate prior calibration. Analysis of earth gradient measurements is shown in Table 1. This table can be more readily understood if Fig. 2 is replaced with its idealized electrical counterpart (Fig. 3). In the first example of Table 1, for instance, cable to C = +0.2 V, cable to A = +0.25 V and cable to B = +0.26 V. So, C to A = 0.25 - 0.2 = +0.05 V and C to B = 0.26 - 0.2 = +0.06 V showing that point C is at higher potential than either A or B, indicating current flowing away from the cable. Due regard must be given, of course, to the sign of the potential. In the third example of Table 1, C to A = 0 - (-0.05) = +0.05 V and C to B = 0.01 - (+0.05) = 0.06 V again indicating current leaving the cable. These measurements need not be



FIG. 2-Use of a single reference half cell for earth gradient measurement.



FIG. 3-Electrical counterpart of earth gradient measurement.

limited to locations near manholes. The tests can be repeated at intervals along the cable.

In towns where streets over the cables are paved it is difficult to find suitable electrode locations. Experience indicates that measurements with high resistance meters can be made through damp asphalt. When the surface is dry a small amount of water is poured in suitably located depressions, providing a good contact point. In some cases the use of a very high input resistance vacuum tube voltmeter or potentiometer type voltmeter is advantageous.

Centralized Testing

Centralized testing facilities comprise equipment at a central location together with test leads or pilot wires to the various points concerned, for making observations of the condition and performance of drainage wires, automatic switches, and fuses. These facilities are used for relatively frequent measurements of cable-to-earth potentials at key points to extend the time intervals between general surveys. Test trunks normally assigned for use in locating cable troubles or for general testing purposes may also be used for centralized corrosion testing.

The resistance of the cable conductors used as a test lead will frequently be several hundred ohms. The measurement of current by drop of potential

Over the Cable (C)	Left of Cable (A)	Right of Cable (B)	Interpretation
+0.2	+0.25	+0.26	Current leaving cable
+0.2	+0.10	+0.11	Current picked up by cable
-0.5	0.0	+0.01	Current leaving cable
+0.01	+0.15	-0.10	Transverse current

 TABLE 1—Interpretation of earth gradient measurements.

 Cable to Earth Potential, volt

method requires a high sensitivity millivoltmeter. A recording type millivoltmeter is preferable for this purpose since the measurements under consideration should cover 15 min or more and at least once a year a period of 24 h.

Permanent assignments are usually made for the relatively short leads required for connection between the point under test and the nearest central office. From the latter point, temporary connections as required are made to trunks already assigned for general testing requirements, when such are available, between the nearby central office and the cable location test desk.

The best results may be expected from the use of separate pairs (from nearby central office to the test points) for the measurements of drainage wire current and cable-to-earth potential, and for fuse alarm circuits. Tests of drainage wire current and operation of fuse alarms where such are involved, may be accomplished over the same pair, provided the fuse is included in the span of the drainage wire used for current measurement by drop of potential method.

The preferred location for drainage wire fuses, switches and protective equipment is on a pole adjacent to the point of underground attachment. However, where the test leads are needed in a manhole, it is often practical to pull a two-pair rubber insulated lead sheathed cable through a subsidiary duct to a nearby terminal. Where this is not practical, a direct connection can be made through a splice in the manhole. In this case provision should be made to insure against moisture leakage into the main cable.

Drainage wire current measurements are important to detect deviations from normal conditions. The following are examples where prompt attention is needed:

- 1. Changes in layout, operation or condition of system.
- 2. Changes in layout or interconnection of telephone cable sheath.
- 3. Blowing of drainage wire fuses and conditions causing such operation.
- 4. Failure of drainage wire switches to operate properly.
- 5. Drainage wire in trouble (for example, corroding).

Although the necessary frequency of tests will be governed by local conditions, they should be made once per month or oftener. At least once a year a 24-h test should be made with a recording instrument.

The principle of the drainage wire current test is that the cable pair from the point under test to the nearest central office will be bridged across a span of the drainage wire, this span being so adjusted as to give direct indication of current at the central testing point. Temporary connections are made to such leads as may be available for this purpose from the nearby central office to the central testing point. Assuming the availability of test trunks from a central cable location test desk, the plugs standard with these facilities will be satisfactory for the temporary connections. There are two schemes for arranging the instruments for direct indication of drainage wire current. Each involves potential drop measured over a selected span of drainage wire. Scheme 1 provides for the same instrument calibration for all of the drainage wires, giving full scale deflection with maximum load on the drainage wire carrying the heaviest load. This, in general, involves: (a) lowest reading scale of instrument, calibrated to give direct reading with; (b) conductor leads of equal resistance (leads of lower resistance padded to reach highest resistance); and (c) equal resistance of drainage wire spans. Item b is determined by the cable conductor leads of highest resistance. Item c is determined by maximum current on drainage wire carrying heaviest load.

Scheme 2 provides for approximately full-scale deflection with each drainage wire under condition of maximum load and correspondingly different calibrations for the different drainage wires. In general this case involves: (a) no adjustment of resistance of cable conductor leads; (b) adjustment of drainage wire span to give approximately full scale deflection with maximum drainage current for the particular case in question, a margin being allowed for abnormal conditions; and (c) different instrument calibration for each drainage wire.

Drainage wire switches must also be kept in normal operating condition. With manually operated corrosion switches, as at power houses, routine checks with a voltmeter are of considerable value. Indication of proper operation of automatic switches can be obtained from a study of the sheath current data.

1. When the switches are operating properly, sheath current will be indicated in one direction only, that is, from the cable to the negative return system.

2. Reverse currents are indications of the switch failing to open as required.

3. Currents of consistently negligible value during periods of the day when drainage current would normally be expected is indication of the switch failing to close as required.

One of the overall checks from central testing points consists of periodic measurements of cable-to-earth potentials at key points such as points near drainage wire attachments. Data from such measurements give an indication of normal operation or departures there from, which may require prompt attention. These tests of cable-to-earth potential, from a central testing point, require the assignment of a pair of conductors exclusively for this purpose between the point under test and the nearby central office. As in the case of current measurements, this pair may be connected for the time being to the regular test trunks to the central testing point. If prefered, however, arrangements can be made for having these cable-to-earth potential measurements made at the nearby central office. In the latter case the conductors concerned are usually terminated at jacks in the local test set.

Remedial Measures

Design of Drainage Wires

To provide adequate mitigation without making the cables excessively negative to earth requires careful selection of the points at which the bonds are made as well as careful adjustment of the resistances of the bonds.

The major points of stray current discharge are generally near a substation where the negative feeders are connected. In some cases negative feeders are connected to the rail some distance away from the substation, creating current discharge points away from the substation. Other points of current discharge are main rail intersections and points where discontinuities, such as changes in number of tracks, occur. This geographical information has to be supplemented with potential survey of cables with respect to earth and rail and the magnitude and direction of current on the cables. In general an anodic area, while it may extend for some distance along the cable run, will be found to center around a point where the cables approach the rails. This is the ideal point at which to make the drainage connection if physical conditions are favorable. Other factors to consider in choosing the drainage points are:

1. Cost (length of wire required, availability of spare ducts, type of pavement).

2. Feasibility of installing reverse current switch if required (dry manhole, pole, substation basement).

3. Cable-to-earth voltage and cable-to-rail (or bus) potential should be closely related in their variation with time (simultaneous readings of these values for 24 h plotted against each other should closely follow a straight line). Bad correlation indicates that the optimum point was not selected and other points should be tested.

Installation of Drainage Wires

In general insulated stranded copper wires are the most satisfactory. Where the wire is placed in ducts belonging to another organization there is a chance that it may come in contact with other structures, thus altering the drainage conditions. In this case lead sheathed conductors may be used. The lead sheath has to be isolated from the telephone cable sheaths but should be protected against corrosion by bonding, through some calculated resistance to the other protected structures.

Later checking is facilitated if solderless connections (that is, lugs bolted together) are used and taped over. At a convenient point in the wire a calibrated voltage drop should be provided for current measurements. Short lengths of bonding ribbon soldered to the wire may be used. When these terminals are soldered to stranded wire the solder has to be allowed to run into the inner strands to avoid change in the "drop" with time.

Fuses in the drainage wire are used where there is equipment in the

drainage connection such as a reverse current relay. Other areas of using fuses are where a small cable crosses an interurban trolley line and is drained to the rails, or when the drainage wire is run aerially on trolley feeders. Fuses should be installed to the cable end of the circuit. The fuses have to be rated well above normal expected currents in order to reduce maintenance.

Cathodic Protection Design from Experimental Reduction Test Data

After a consideration of all the factors in a corrosion situation indicates that some form of forced drainage (cathodic protection) is likely to be the most practicable remedial measure, a field survey should be made to determine by experiment what arrangement will provide adequate and economical protection. Information should be obtained to determine:

- (a) The physical layout of all subsurface structures and rail systems in the area involved, even at some distance from the cable plant.
- (b) If a single drainage or multiple drainage will be required.
- (c) The effects that may be expected per ampere of drainage current.
- (d) The effects on other subsurface structures and rail systems of any drainage proposed.
- (e) Suitable anode locations; the size and resistance of each anode and the ease of constructing these, unless use is to be made of an existing structure such as an abandoned pipe, etc.
- (f) Size of, available routes for, and methods of placing drainage wires.
- (g) External power supply requirements.

Testing Procedures

Testing procedures will depend on local conditions. The same testing methods are applied for single or multiple drainage systems. In the latter case the overlapping effects of the different drainage points also have to be established. Except in the case where a duct survey is included, the data obtained for cables usually are restricted to manholes or test points. Occasionally measurements can also be made on the ground surface over the cable between manholes or test points. This can be done with a copper/ copper-sulfate half cell attached to a long insulated wire lead. The voltmeter connected between the cable and half cell all should have a sensitivity of 50 000 ohms/V and preferably 200 000 ohms/V or greater.

After a suitably located anode site has been selected a temporary anode (made of ground rods) for delivering test current to earth has to be constructed. First sheath current and sheath potential values, with respect to earth and other structures, have to be established. The reduction test consists of determining the change in potentials of cable sheath to earth, and to any neighboring metallic structures, per ampere of drainage current. They have to be made for sufficient distances each side of the drainage point to determine the extent of effect of the particular drainage. The power for temporary drainage installations is obtained from storage batteries or from a portable generator.

In making the reduction tests it is not necessary to increase the drainage current to a value which will make the cable sheath negative to earth at all locations. Sheath to earth voltage readings should be taken with and without the experimental drainage operating. if there is any fluctuation in the normal sheath to earth voltages, at least 10 readings should be taken and the results averaged. Observations should be made at key points (points of highest positive potential without drainage). From the data taken, the reduction of sheath to earth voltage per ampere of drainage current can be determined for each point tested. Then the amount of drainage current to eliminate all the positive conditions can be calculated. On plain lead cable sheath the voltage change per ampere of drainage current is fairly constant over a wide range of current. Polyethylene jacketed lead sheaths are not constant in this respect and several values of test current should be used and the results plotted to establish the final value of drainage current.

Where other metallic structures are within the area of influence of the drainage, the reduction test data should include the change, per ampere of drainage current, in the potential of such structures to earth and in the current flowing in them.

Cathodic Protection Design by Estimation

The effects of cathodic protection on long uniform cables (intercity toll cables) can be estimated from a few basic data. The information to be obtained and the testing procedures in a field survey are similar to those in the previous section.

1. "Megger" ground tester 3-point method.

2. Delivering $I_A = 200$ mA d-c current to an electrode 50 ft to one side of the cable. With the circuit first open and then closed, the sheath to earth voltage change (V_o) , to an electrode 150 ft to the opposite of the cable is measured.

3. Draining I_A amperes to a trial anode at least several hundred feet from the cable and measuring the sheath to earth potential change (V_o) at the drainage point. The electrode to measure V_o is placed as in 2 above.

In cases 1 and 2 the cable leakage resistance to earth is:

$$R_L = \frac{4}{R_S} \left(\frac{V_o}{I_A} \right)^2 \tag{2}$$

where R_s is the series of longitudinal resistance of the cable.

Electrolysis Switch

The electrolysis switch is intended for use in drainage connections where reversals in the direction of current are encountered and an automatic switch is desired. It is a device that closes a low-resistance connection (drainage bond wire) to drain stray currents from underground cables to a railway substation ground (negative bus). It also opens the connection to prevent the flow of current from the drainage point to the cable when the potential reverses.

When the cable-to-bus potential is positive and high enough in value to cause sheath corrosion, the switch closes the bond. The switch can be adjusted to separate at any desired potential between +0.15 to 0.40 V. When the current decreases to zero or near zero, or when the potential reverses, the switch is opened automatically.

Electrolytic Capacitor

In corrosion areas where insulating joints are employed to isolate underground or buried cable sheath from aerial cable sheath, it is necessary to leave a low impedance ground on the aerial cable to discharge fault currents and maintain satisfactory noise levels. This may be obtained by bonding the aerial cable sheath to a multigrounded neutral of a power distribution system or a metallic water pipe system.

Where aerial cables are not grounded to a power neutral conductor or a water pipe, a capacitor may be bridged across the insulating joint to provide a-c continuity for noise suppression or protection reasons.

There is a choice of two capacitors, $1000 \ \mu\text{F}$ and $10\ 000\ \mu\text{F}$ type, both of them are 25 V dc, nonpolarized dry electrolytic capacitors. Both are intended for operation in circuits where the d-c potential will not exceed 25 V and where the a-c potential will not exceed approximately 2.5 V rms at 60 Hz.

These capacitors may be connected without regard to polarity of the d-c voltage. The d-c blocking characteristic of the capacitors is dependent upon the build-up of an oxide film on the electrodes. When the d-c potential across the capacitor is suddenly reversed, direct current flows through it for a short time; however, the capacitor will quickly recover and block this current. In stable condition, leakage current of less than 2 mA is expected with 25 V across the capacitor.

The electrolytic capacitors can provide a low impedance for bridging insulating joints in all cables including carrier and video cables where suppression of voice frequency or carrier frequency noise is necessary. At carrier frequencies, if the length of the leads from the capacitor are more than a few inches, they may have objectionable impedance even though the d-c resistance is negligible.

Tests have indicated that to maintain circuit noise limits at frequencies up to 4 MHz the capacitor leads must not exceed about 4 or 5 in. in length.

The electrolytic capacitor can withstand as much as 250 A ac for several seconds; therefore, breakdown of the capacitor from contact with a power circuit is not expected to be a problem.

Testing capacitors, with an ohmmeter, for an open circuit or a short circuit should be necessary only where measurements indicate unsatisfactory noise levels or where potential measurements show an increase in the corrosion exposure of underground or buried cable.

Central Office Equipment

Central office equipments are primarily made up of small electronic components. Although the fact that they are located in a building in more or less controlled environment, does not exclude the possibility of corrosion. It is important to keep in mind that in central office equipment even microgram quantities of corrosion products can result in premature failure. Experience has shown that the best and ultimately the least expensive time to stop corrosion of electronic equipment is at the design stage. This means that the corrosion mitigation of central office equipment is first and foremost based on the proper material selection and the exclusion of false economy of applying less material than necessary.

Stress Corrosion Cracking

Some metal alloys are susceptible to stress corrosion cracking, under applied tensile stresses or residual stresses developed during manufacture, when exposed to a specific environmental contaminant or combination of contaminants. An example is a nickel containing ferrous alloy used for leads in glass sealed semiconductor devices. Both stressed unplated and gold plated alloy leads fail rapidly in cycling temperature—high humidity conditions. Stress corrosion cracking of this alloy can be avoided by electropolishing the lead and plating with solder of sufficient thickness to be nonporous. Complete isolation of the lead from the environment is accomplished by applying silicon varnish to the lead where it enters the glass.

Another example is nickel brass (nickel silver) in wire spring relays, stress corrosion cracking by ammonium nitrate bearing dust where the humidity is high enough to allow moisture absorption by the dust. Experience showed that cupronickel alloy is essentially immune to stress corrosion cracking under similar conditions, therefore, a change in material was necessary. Other means of control for existing relays with nickel brass are air filtration and humidity control in central offices where failures occurred.

Corrosion of Plated Metals Used for Electrical Contacts

Plated silver, either alone or as an underplating for gold, readily forms a sulfide film with sulfur-bearing compounds in the air. Contact resistance problems arise with this kind of plating if the contact forces and open circuit voltages are low. When silver is used as an underplating for gold the sulfide film develops at pore sites and ultimately creeps over the gold surface.

Thin and porous or otherwise discontinuous gold plated over copper or a copper alloy results in formation of copper oxides and sulfides, leading to contact troubles.

The examples of silver and copper underplates illustrate that porous or otherwise damaged gold plating leads to contact resistance trouble. If the problem is to be solved with an underplating, this material cannot be less noble than gold or the gold must be nonporous.

If silver is plated on conductor paths, or on contact fingers of printed circuit boards of either plastic or ceramic material and d-c potential and high relative humidity are present, the silver can migrate along the surface to an adjacent conductor of opposite polarity or even through phenol fiber insulators to create a dendritic growth. Silver plating under these conditions cannot be used.

A good portion of the corrosion problems of central office equipment is due to manufacturing, shipment and storage. High humidity and airborne contaminants from nearby electroplating shops can cause corrosion. Mechanical damage of platings can render them discontinuous. Cardboard packing materials contain about 0.5 weight percent free sulfur which can form sulfide film on silver and copper under porous gold. Packing in raw wood may lead to corrosion by organic acids (generally acetic) of central office equipment.

Some corrosion problems can be traced to the materials used within the equipment. Adhesives may give off vapors corrosive to many metals found in central office equipment.

A typical example was the corrosion of nickel underplating at the bases of pores in a thin ($\sim 0.5 \ \mu m$) rhodium finish on printed wiring board contact fingers. On the other hand a thicker ($\sim 3.0 \ \mu m$) gold finish on a contact spring on the same board protected the underlying metal from corrosion because it was essentially pore free.

Other potentially corrosive materials commonly used in central office equipment include resins, plastics, elastomers and organic finishes. One of the most potentially dangerous, widely used materials is soldering fluxes, containing activating agents, such as chlorides.

Such widely used metallic finishes as tin (maintain solderability), zinc and cadmium (sacrificial corrosion protection), are prone to grow metallic whiskers which can short out closely spaced circuits. Addition of lead to tin and reflowing after electrodeposition appears to prevent whisker growth. An exception to this latter preventive method is when the part is under compressive load.

Chapter 7

Corrosion Standards and Control in the Marine Industry

B. F. Brown¹

The operation of a ship involves many of the technologies required for the functioning of an urban society: generation of electric power; storage and preparation of food; dispensing of health services; furnishing heating, ventilation, and air conditioning; and in some instances operating nuclear power plants and aircraft. Thus, the corrosion control measures needed in the marine industry include many that have been developed for other industries unassociated with the marine environment. In addition, special measures are required because of the special corrosive nature of sea air and seawater. It is these specialized measures which form the subject of this chapter. (For example, corrosion control measures for steam generation are not discussed because the subject is included in the chapter on that technology.)

The special corrosivity of seawater and sea air is due of course to the presence of the chloride ion in high concentrations. This ion is small, it can diffuse rapidly, it confers on the electrolyte high electrical conductivity, and when involved in hydrolysis reactions it can provide localized acidity and thereby oppose passivation of metal surfaces. The ratio of dissolved solids in sea water is about the same regardless of geographic location, but the concentration may differ considerably. There are not enough systematic long term corrosion rate data to establish whether the corrosivity of sea water in different locations differs to an important degree in an engineering sense. Nevertheless there have been enough observations reported to lead many corrosion engineers to conclude that waters with higher oxygen content (such as the cold waters of the polar sea) are more corrosive to steel and require more cathodic protection current than water lower in oxygen. But metallurgical differences, such as as-extruded surfaces of an aluminum alloy compared with as-rolled or machined surfaces of the same alloy, influence corrosion behavior much more drastically than geographic differences.

The corrosion characteristics of the steel hulls of modern merchant and

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naval ships do not differ importantly from those of the wrought iron of the *Monitor* of Civil War days. What is comparatively new in this respect is the realization that protection against corrosion roughening is important to the operating costs of merchant ships, and similar protection is important to the maintenance costs of naval ships. This realization has been associated with new developments in cathodic protection technology since World War II, and these developments have given the marine industry important tools for the control of marine corrosion.

Military considerations have tended to cause metallurgical developments in marine technology ahead of their need or adoption by merchant ships, though this is not universally the case. It is not surprising therefore that most of the standard specifications cited in this chapter are Military Specifications, abbreviated as MIL-... Some of these specifications are appropriate for merchant ships as well as naval ships; in some cases these specifications. Reference I should be consulted as the classic treatise on economic considerations in the selection of materials for marine applications.

The structuring of the presentation of material in this chapter posed problems because the lack of sufficient data and standards to organize sections parallel in nature. One section treats cathodic protection especially as it is applied to unalloyed or low alloy steel hulls because that is where the emphasis has been placed in technology development. Another section treats aluminum alloys because they are both important to marine technology and vulnerable to special corrosion hazards in seawater. Still another section treats certain corrosion processes (corrosion fatigue and stray current corrosion) because they are serious present-day marine corrosion problems for which standard control methods are lacking.

In addition to the formal standards for the control of marine corrosion, there is a body of knowledge of corrosion technology available in printed form (see for example Refs 2 and 3), although this information is far skimpier than is sometimes supposed and much of the data present difficulties in interpretation. In addition to this body of knowledge in printed form, there is a great deal of marine corrosion information which exists only in the oral tradition, some of it exchanged annually at the unique institution known as the Seahorse Institute of the Francis L. LaQue Corrosion Laboratory of the International Nickel Company. The availability of this written and unwritten body of information is cited to emphasize to any newcomer to this literature that although formal standards for corrosion control are far from complete, there is much marine materials engineering knowledge available to supplement them.

Cathodic Protection

The past twenty years have seen significant advances in the technology of cathodic protection of hulls and other underwater structures; they have also seen major increases in the utilization of this technology for naval and merchant shipping and also for offshore oil well towers. During the same period there have also been many advances in the technology of organic coatings for marine service. The combination of modern organic coatings and modern cathodic protection technology gives the marine corrosion engineer much better control over the corrosion problem than was possible prior to World War II.

Many corrosion engineers believe that it is more than coincidence that the paint systems on cathodically protected (but not over-protected) surfaces perform better and last longer than on unprotected surfaces. Certainly cathodic protection of large areas is not economically sound unless these areas are coated. Thus there is a direct connection between coating technology and cathodic protection technology. The technologies of surface preparation, primer formulation, anticorrosive paint formulation, and removal of fouling organisms from merchant hulls are in a state of dynamic development. Reference 4 is a recent authoritative and exhaustive review of these technologies. It is to be understood that many developments in these technologies are made quite some time before they are accepted in the MIL specification and Federal specification system. The following specifications relate to surface preparation, coating formulation, and application (in the case of galvanizing).

Subject	Specification	
Abrasive materials for blasting	MIL-A-21380B; MIL-S-22262	
Solvent cleaning compound for grease removal	MIL-C-20207C	
Pickling inhibitor for use with sulfuric acid	Fed Spec 0-1-501B	
Primer pretreatment, Formula 117 for metals	MIL-P-15328B	
Shipboard primer coating and anticorro- sive paint, vinyl-red lead for hot spray	MIL-P-15929B	
Shipboard primer coating, vinyl-zinc chromate for hot spray	MIL-P-15930B	
Steel ship maintenance primer coating, alkyd-red lead type	MIL-P-18994A	
Alkyd zinc chromate primer	Fed Spec TT-P-645	
Zinc chromate anticorrosive	MIL-P-15184	
Hot plastic antifouling	MIL-P-19452	
Cold plastic antifouling	MIL-P-19449A and 19451A	
Polyisobutylene antifouling	MIL-P-22299A	
Hot dip galvanizing	MIL-Z-17871	

There was much confusion over the true electrochemical characteristics of various galvanic anode alloys until experiments were conducted on full size anodes working at current densities approximating reasonable service conditions in full salt seawater. The results of these tests [5-7] showed the shortcomings of small scale laboratory tests and led to the development of MIL-A-18001 G and H specification for zinc anodes. Instead of high purity with respect to all elements, this specification calls for the alloy to contain 0.025-0.15% Cd, 0.10-0.50% Al, and the following maximum limits: 0.006% Pb, 0.005% Fe, 0.005% Cu, and 0.125% Si, balance Zn. Within this specification there are various classes and types which specify the presence or absence of cores, and various anode shapes and sizes. This specification has been conspicuously successful in producing anodes which have nearly 100 percent theoretical efficiency plus dependable freedom from going passive. These anodes are used on both steel and aluminum hulls.

MIL-A-21412 specifies the composition of the alloy for magnesium base anodes: 5-7% Al, 2-4% Zn, 0.15% Mn (minimum), and the following maximum limits: 0.3% Si, 0.1% Cu, 0.003% Fe, 0.003% Ni, and 0.3%other, with the balance being Mg. As with zinc anodes, there are numerous types which specify size, shape, and the presence or absence of a coating. At one time there were experimental installations of magnesium anodes on bilge keels, with some of the anodes left coated at the time of undocking in order to extend the life of the installations; these coatings would be cut off by a diver as other anodes became consumed. A dielectric shield is recommended extending 2 ft around each magnesium anode to avoid unduly high currents in the immediate vicinity of the anode. This shield should be a coal tar epoxy coating conforming to MIL-P-23236 (Type I, Class II). Magnesium anodes are preferred over zinc or aluminum anodes for high resistivity brackish or fresh water.

Both zinc and magnesium anodes have been used for partial cathodic protection systems (around propellers) and for full protection of the entire hull, and the use of both has been demonstrated to save maintenance costs. Aluminum base anode alloys are attractive because of the high theoretical capacity as well as possibly desirable electrochemical potential characteristics. Indeed, numerous offshore structures employ aluminum alloy anodes, though whether these alloys are functioning with the expected electrochemical efficiency in all installations is unknown. At this writing there are proprietary aluminum alloy anodes [8,9] which appear to have desirable characteristics, and a military specification is presently being prepared for this family of alloys.

Galvanic anodes are recommended for mounting within fairings of strut bearings and stern tubes to the extent of space available. Because of hydrodynamic considerations they are not attached to propellers, shafts, rudders, or strut barrels.

Zinc anodes are recommended for bilges which are wet more than half the time. Other applications of galvanic anode systems are discussed in conjunction with condensers and salt water piping. One of the perennial problems with the use of galvanic anodes around ships is the tendency for paint crews to paint the anodes, even sometimes when the admonition DO NOT PAINT appears on the surface of the anode casting. Positive action such as taping a protective layer of paper over the anodes can keep paint off. The paper will come off the anode upon undocking if no one remembers to remove it after painting.

Impressed Current Systems

Galvanic anodes have the advantage of low capitalization and simplicity (they cannot be connected backwards, a distinct advantage where small boats are maintained by a small crew with scant training and rapid turnover). If they are procured according to the specifications given above, experience has shown that they will not go passive; if they are attached to a metal structure in sufficient number and if there is a sufficiently low resistance electrical path to that structure, they are effective. Navy data have shown that their use saves money. However, if shore or shipboard power is available, and if well trained electrical crew members are available, as on larger ships, impressed current systems are preferred.

During the 1950s impressed current cathodic protection systems were developed to control the potential of a ship hull at a predetermined value. It is the *potential* of a metal surface, not the current density flowing into it, which determines whether the metal corrodes or not. These potential control systems—gigantic potentiostats—have been used largely for either unalloyed steel hulls or for hulls low in alloying elements, although at least one small Navy hydrofoil having an aluminum hull has been fitted with a small scale model of the same type of controller. Potential control units suitable for small boats are available commercially.

The potential prescribed for steel hulls in seawater is 0.85-1.0 V negative to Ag/AgCl (in seawater essentially identical to SCE). In high resistivity water the allowed range is expanded to 0.75-1.0 V.

On active ships the shipboard power is rectified and conducted to anodes, usually platinized titanium (though platinum, lead-platinum, lead-silver, tantalum, and niobium have been used). A dielectric shield of coal tar epoxy (MIL-P-23236, Class 2) 22-mils thick is laid on the steel hull 4 ft around an anode with up to 12 V between anode and hull, or 6 ft if the voltage exceeds 12. The preferred potential is -0.85 ± 0.02 V (Ag/AgCl), and a good system should provide this at speeds up to 25 knots.

The reference electrode used to monitor the potentials of active ship hulls is the Ag/AgCl electrode (MIL-E-23919). Two or four such hullmounted electrodes are used depending upon the size of the ship, located port and starboard at least 5 ft below the waterline. The Ag/AgCl reference electrode is for use only in seawater.

On active ships the propeller shafts are grounded to the hull using a

silver-graphite brush and a hard silver plate. The rudder is also grounded to the hull.

Potential control impressed current cathodic systems have also been used for laid-up ships with great success (except for an unfortunate instance of reversed polarity). In this case shore power is rectified with selenium rectifiers and is led to anodes which, unlike the case of active ships, are suspended in the water around the ship but at some distance from the hull. These anodes may be of silverized lead (MIL-A-23871) if the site is essentially full salt seawater. It is essential to have a *minimum* current density of 1 A/ft² coming out of the silverized lead anode surface to preserve the brown peroxide coating necessary to maintain the integrity of the anodes. Lead-antimony-silver alloys have also been used. Typically the lead-rich anodes are 0.5 in. in diameter by 72 in. long (maximum current 8 A) or 0.75 in. in diameter by 72 in. long (maximum current 15 A).

Graphite anodes (MIL-A-18279) are used for laid-up ships in both salt water and fresh water. The maximum current density of a 3- by 60-in. cylindrical graphite anode is specified to be 10 A in salt water, and 5 A in fresh water. (Graphite anodes have been used on at least one active ship, but mechanical breakage was a problem.) At fresh water sites Ag/AgCl reference electrodes are not used, but $Cu/CuSO_4$ electrodes are used instead.

Perhaps it should be noted in passing that the leading aluminum-base anode contains traces of mercury, and that the ecological effect(s), if any, of this mercury, of the cadmium in the standard Navy zinc anode alloy, and of the lead in the silverized lead alloys may ultimately cause a shift in the use of standard alloys.

Internal Salt Water Circuit

Salt Water Piping Systems

Zinc anodes are recommended for protecting sea chests. If the sea chest is steel and the valve is nonferrous, a waster sleeve of mild steel is recommended as additional protection. In the specified iron-bearing cupronickel piping (either 70-30 or 90-10) the maximum flow rate is limited to 15 ft/s. Corrosion and erosion-corrosion are minimized by having minimum flow rate and by eliminating air. During idle periods (one week or more in duration) the system should either be drained or else operated daily. Protective spools are neither specified nor desired for either ferrous or nonferrous systems.

Mixed nonferrous and ferrous systems should be designed to include a 24-in. (12-in. minimum) waster piece of extra heavy galvanized steel on either side of the nonferrous section, connected in such a way as to afford easy removal. There is no problem in mixing 70-30 with 90-10 cupronickel, but 90-10 should not be used to replace 70-30 in main condensers equipped with solder-coated water boxes. In general, however, 90-10 is preferred to
70-30 because of cost differential except as noted above and where the additional strength of 70-30 is needed.

For protection against galvanic corrosion in stagnant (<5 knots) areas in such systems as bilge pump strainers and valves, involving mostly stagnant conditions and various combinations of steel, stainless steel, and bronze, etc., one rule of thumb is to attach a zinc anode to provide 1 ft² of zinc for each 50 ft² of bare metal to be protected.

Flooding due to rapidly corroding ferrous plugs in copper-base piping continues to occur.

Condensers and Other Salt Water Heat Exchangers

As with so many components and structures, corrosion control measures involve design, material selection, fabrication, and maintenance. Designs avoid erosion-corrosion by attention to the configuration of waterboxes and injection piping. General specifications require designs to limit the flow rate of either seawater or brine to 15 ft/s for both 70-30 and 90-10 cupronickel to minimize erosion-corrosion.

The waterboxes on combatant ships are of Monel² alloy 400 with the water side coated with solder (two-thirds lead, one-third tin) to minimize galvanic attack on the tube sheets and tubes themselves. Cast iron or steel waterboxes on noncombatant ships are abrasive blasted and coated with a coal tar epoxy equivalent to MIL-P-23236, Class 1, 2, or 4.

The cupronickels used for salt water piping contain iron which is thought to improve the integrity of the corrosion product layer which controls the corrosion of the underlying metal. There are a few seawater condensers into which iron compounds are deliberately introduced periodically to assist in maintaining a protective film. It is believed that initially operating a cupronickel condenser in badly polluted water seriously hazards the development of a satisfactory protective coating. Indeed standard practice for a condenser of any age is to avoid operating in polluted water if at all possible.

During shutdown there is a tendency for seawater to pocket, especially in sagging tubes. Such pocketing causes serious corrosion which can be avoided by washing with fresh water and then drying out (using an air lance to empty sagging tubes, for example). If the condenser cannot be completely dried out during shutdown, it should be filled completely with fresh water.

Stones, pieces of wood, shell, etc., lodging in condenser tubes cause pitting corrosion. They are removed periodically by use of a water lance, soft rubber plugs driven through by an air gun, or a rotating bristle brush. Wire brushing and abrasive cleaning of condenser tubes are specifically prohibited, since that would remove all protective coating.

² Monel is a registered trademark of the International Nickel Company.

Attention to the upkeep of the ship's electrical system should eliminate serious condenser tube corrosion due to stray currents.

Zinc anodes were formerly mandatory on the seawater side of condensers, but many such installations have now been eliminated. These "protector plates" were sized to give a zinc area $Z = 0.078 (0.75 D^2 + 6Nd^2)$ where D is the diameter of the tube sheet, N is the number of tube ends exposed, and d is the inside diameter of the tubes. The zinc when used must conform in composition to MIL-A-18001. It is recommended that the zinc surfaces be inspected at 90-day intervals to ensure that they are active, though it is unlikely that they will be otherwise if the material actually conforms to MIL-A-18001. If the zinc becomes filmed and inactive, it should be wire brushed. The cathodic protection afforded by these zinc anodes does not extend down the tubes more than a few tube diameters if the seawater is flowing, but it is of some help in mitigating the erosioncorrosion near the tube inlet end, though incompletely so. Plastic inserts were tried as protectors in this area, but their use has been largely discontinued.

Oil coolers when out of service more than 24 h should have the seawater drained, and should then be flushed with fresh water and dried.

Special Forms of Marine Corrosion

Stray Current Corrosion

This form of corrosion is probably more widespread than is commonly realized because of the difficulty in identifying it except in the more severe cases. It is recognized as a hazard around cathodically protected structures in seawater and also especially if welding is done where the welding generator is not mounted directly on the ship or structure being welded. These hazards have led to the following standard practices.

No unprotected ship should be moored in a group of protected ships. The reason for this rule is that the unprotected ship represents a low resistance path in a higher resistance electrolyte carrying an electric current. Kirchoff's law is obeyed, and part of the cathodic protection current enters one part of the ship (causing no corrosion) and exiting at another point (causing much corrosion). The unprotected ship then functions as an intermediate electrode. For exactly the same reason a steel camel should be electrically bonded to an adjoining protected ship.

Welding generators should be mounted directly on the ship or structure being welded. The reason is that if the generator (d-c rectifier) is located on shore, an enormous d-c current will run from ship to shore during welding, far too large a current for a cathodic protection system to overcome. Running a d-c grounding cable ashore is of little value, since the total resistance of the large cross section electrolytic path is small compared to anything less than an enormously large cable, and again Kirchoff's law is obeyed. At the present time we do not know whether a-c fields accelerate corrosion of the various structural alloys in seawater.

Corrosion Fatigue

The most common form of fracture failure in ships is corrosion fatigue. One might wonder therefore why there are no standard corrosion fatigue tests and why the designer apparently pays little attention to corrosion fatigue data. The reason is that the designer seldom knows the algebraic sum of residual plus working stresses, and he does not know whether the order of merit in one corrosion fatigue test is the same as in a different test. A typical engineering solution to a corrosion fatigue problem is exemplified in the following procedure for avoiding corrosion fatigue in propeller shafts: the steel is protected against the electrolytic action from the bronze propeller and bronze bearing journal sleeves by a rubber or plastic sheath over the steel. Seals and rust preventive compounds are used to prevent the entry of seawater under the sheath. The ends of shafts are plugged to prevent internal corrosion.

Corrosion fatigue is not the only serious consequence of corrosion lacking a formally accepted test procedure. The same is also true of stress corrosion cracking, erosion-corrosion, hydrogen embrittlement, crevice corrosion, pitting, and even general corrosion in seawater. Neither are there clear cut procedures for interpreting the results of most of the marine corrosion tests now in use for purposes of design of fundamentally new structures or of using fundamentally new alloys. Unfortunately there are very few laboratories so sited and staffed as to be able to correct the foregoing deficiencies in the near future.

Aluminum Alloys

Although aluminum-hulled boats were built before the end of the 19th century, aluminum continues to give serious corrosion problems in marine service, even with the ailoys which are resistant to stress corrosion cracking and to exfoliation. The reason is that the metal is fundamentally active, and the protective oxide which coats it is more easily broken down chemically and is less readily repaired than the oxide coating on say titanium.

The common alloys for boat hulls are 5086 or 5456. For piping and railings 6061 is used. 5083 and 7039 have been used in limited quantities for atmospheric service. The alloy 5086 is bought to an interim Federal specification (QQ-A-00250/19 of 11 Dec. 1968) which requires each production lot to be checked metallographically for evidence of susceptibility to exfoliation. If the candidate lot is predominantly free of a continuous grain boundary network and the microstructure is equivalent to or "better than" a reference standard, no further testing is required. If the candidate lot fails this check, then specimens from the lot must successfully pass the standard salt water acetic acid test ("SWAAT") in order to qualify. The

same specification applies to the 5456 alloy. It should be emphasized that this is a dynamic technology area.

One of the first rules in using aluminum successfully in seawater is to avoid machining the as-rolled or as-extruded surface if at all possible. The machined surface corrodes far worse than the unmachined. The second rule is to avoid using steel wool or wire brushes (other than stainless) on aluminum; sanding may be done if needed, but avoid using abrasive disks or other nonmetallic scouring pads which have been used to remove paints which contained copper or mercury antifouling compounds. Wood or plastic scrapers are to be preferred.

The most common causes of galvanic corrosion problems in aluminum in ships are placing an aluminum deckhouse on a steel support and attaching steel or copper-base alloy fittings to the hull or to the piping, or both. These more noble metal fittings should be electrically insulated from the aluminum; even so, waster-plate practice is recommended. Cathodic protection is recommended where copper alloys are involved even though the copper alloy is electrically insulated from the aluminum, for there is a degrading effect from simple proximity of the copper alloy to the aluminum alloy.

Unlike steel, aluminum cannot be made thermodynamically stable in seawater by cathodic protection methods. Nevertheless, cathodic protection is highly effective because it counteracts any tendency toward localized hydrolytic acidification with its attendant breakdown of passivity. Only zinc (MIL-A-18001) and certain aluminum-base galvanic anodes are permitted, magnesium anodes and mercury-bearing aluminum anodes being prohibited for aluminum hulls.

Cleanliness is always important, as both solid particles and grease marks invite localized hydrolytic acidification and consequent local film breakdown. Regular fresh water wash down of decks and bilges is helpful in removing solid debris and also in keeping down the concentration of chloride which plays an essential role in hydrolytic acidification.

Paint coatings play an important role in controlling hull corrosion. It is standard practice to have a 2-mil primer, followed by a 2-mil antifouling paint containing neither copper nor mercury. One of the organo-tin compounds is presently the preferred toxicant in antifouling paint for aluminum hulls.

Where there are threaded bolts or fittings of aluminum exposed to seawater, the use of 50 percent zinc dust in petrolatum may be used on the threads as an anti-seize lubricant. Graphite, lead, or tin bearing lubricants must be avoided. Stainless steel lock nuts and washers are usually acceptable on such aluminum components.

Standard stipulations for aluminum alloys for marine *atmosphere* service call for "stress-corrosion resistant alloys" without, however, specifying the test. Where cadmium-plated steel bolts or nuts are used with aluminum

alloy parts, they are preferably isolated from the aluminum with aluminum alloy washers under the bolt head and nut; but cadmium-plated washers may be used for bolts under high tension. The usual precautions of minimizing stress concentration, using shot peening and stress relieving, are recommended where feasible to minimize stress corrosion problems. In highly textured alloys a rule of thumb is to keep working stresses in the longitudinal direction less than 50 percent of the yield, 35 percent in the long transverse direction, and 25 percent in the short transverse direction. Faying surfaces should be filled with sealing compound. Aluminum hulled boats should be provided with nonconducting mooring lines when next to steel ships and steel piers, and insulating camels should be used.

Marine Structures Other Than Ships

The corrosion control technology of offshore structures tends to make use of developments in corrosion control for ships. The potential-control impressed current cathodic protection controller for protecting the tower known as "Argus Island" near Bermuda was derived from the controller originally developed for Navy ship hulls. Many offshore towers and ancillary components are protected by galvanic anodes previously proved out on ship hulls.

Note

The military specifications applying to the marine environment are developed by the U.S. Navy and may be requested from the Naval Publication and Distribution Center, 5801 Tabor Ave., Philadelphia, Pa.19120.

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Chapter 8

Corrosion Standards and Control in the Nuclear Power Industry

W. E. $Berry^1$

The first commercial nuclear fuel power plant in the United States was the Shippingport Atomic Power Station (PWR) that commenced operations late in 1957. Despite the brief existence of this industry, there have been a number of standards promulgated and adapted to meet the industry requirements. The need for standards in this field is emphasized by the high performance requirements and the necessity for overdesign to insure safety and prevent ecological damage.

In the areas of corrosion control, two standards have been issued that relate directly to corrosion testing (ASTM G 2–67 and NACE TM-01–71) and a third is about to be issued (NACE). However, a number of standards have been issued with special corrosion requirements or have been adapted to contain these requirements. In addition, many existing standards on corrosion have been adopted *in toto* for nuclear-industry applications.

The primary sources of the standards are: (1) U.S. Atomic Energy Commission Division, Division of Reactor Development and Technology (RDT); (2) American Society for Testing and Materials (ASTM); (3) National Association of Corrosion Engineers (NACE); (4) Military and Federal Standards and Specification (MIL, FED); and (5) American Society of Mechanical Engineers Pressure Vessel Code Material Specifications (ASME).

The ASTM recommended practices are well known in the scientific community. The NACE has recently begun to issue standards to insure that the field of corrosion is adequately covered. The issuance of standards by the AEC-RDT to provide assistance and guidelines is a natural consequence of the AEC being a tax-supported regulatory body. The military and other branches of the Federal Government have long issued specifications and standards as necessary to the conduct of their operations. The ASME material specifications recognize corrosion and are more indirectly applicable to corrosion in the nuclear power industry than are the other sources.

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Background

Before embarking on a discussion of the use of standards in the nuclearpower industry, it is imperative that a brief description be given of the characteristics and problems of the industry. Since the industry is less than two decades old, new problems are continually arising as more stations are put in service and experience is gained with older stations. Thus, the critical corrosion problems of today may be superceded by other critical problems in the future as the current problems are solved and new ones emerge.

At present, the nuclear power industry is based on the water-cooled reactor concept. These are low-temperature (~ 260 C) units that generate steam at pressures less than 1000 psi. They employ thermal neutrons (<1 MeV) to sustain nuclear fission and consume fissionable material. A concerted effort is now under way to develop a liquid metal (sodium) cooled breeder reactor that will generate steam at higher temperatures (~ 540 C) and possibly higher pressures. This reactor will employ fast neutrons (>1 MeV) and will breed fissionable material. Sufficient experience has been gained with the liquid-metal cooled reactors that many of the corrosion problems are well known, and corrosion control standards have been issued or are being issued.

Both the water and liquid-metal cooled reactors rely heavily on stainless steel for piping, valves, pumps, vessel linings, and heat exchangers. Other materials in common may include zirconium alloys, uranium-oxide fuel, and low alloy or carbon steels. Thus, many corrosion problems that arise as the result of cleaning, pickling, fabrication, and plant erection are common to the two types of reactors.

A current problem in reactor construction is the possibility of intergranular attack or stress-corrosion cracking of sensitized austenitic stainless steel. The sensitization occurs in stainless steel components attached to carbon steel vessels that must be stress relieved to meet code requirements. The stress-relieving temperature is \sim 650 C which results in heavy chromium-carbide precipitation at grain boundaries and sensitization of the stainless steel. Laboratory studies have shown that moisture and the fluoride ions from fumes or spatter produced by welding with coated electrodes can cause intergranular attack of unstressed specimens and stresscorrosion cracking of stressed specimens of sensitized stainless steel [1].² Nickel-chromium-iron alloys do not exhibit this behavior. Furthermore, it has been shown that sensitized austenitic stainless steel (Type 304) will exhibit stress-corrosion cracking in a marine atmosphere [2]. Since both of the above conditions may be present at a nuclear power plant construction site, measures must be taken to either eliminate or avoid the problem. Sensitization is also a problem if the component is subsequently cleaned or

² Italic numbers in brackets refer to references listed at the end of this chapter.

pickled in strong acids such as HNO_3 -HF. Intergranular attack many mils deep has been produced under these conditions and the attack led to stress-corrosion cracking failure in service [3].

Heavily sensitized stainless steel components have failed by stresscorrosion cracking in boiling-water reactors particularly at high stress loadings and when the oxygen content of the water was abnormally high [4-7]. Presumably highly stressed sensitized stainless steel would also exhibit stress-corrosion cracking in pressurized water reactors if there was a prolonged incident of high oxygen in the coolant.

Chlorides can also cause cracking of carbon steel boiler components under certain conditions. Ferric chloride has produced transgranular cracking of mild steel in aqueous solutions at 316 C [8]. Ferric chloride can be produced by the periodic introduction of air into boiler water that contains chloride (by such practices as uncontrolled shutdown of boilers over weekends).

Carbon- and low-alloy steel components are also susceptible to rusting and pitting corrosion during transfer and storage unless they are purged and contain a desiccant to maintain low humidity and are sealed to prevent ingress of high humidity air. Failure to remove rust prior to operation can lead to pitting when the unit is operated with water or steam at high temperatures. During down time, air must be excluded from carbon steel units if they remain wet to avoid pitting.

The principal corrosion problems associated with the operation of water-cooled reactors are discussed in Ref 9 and include stress-corrosion cracking of sensitized stainless steel (see preceding paragraphs), chloride or caustic cracking of rolled in heat-exchanger tubes, localized attack of Zircaloy cladding due to fluoride contamination or localized concentration of caustic materials used to treat the primary coolant, the corrosion of condenser tubes, and the formation and transport of crud (stainless steel corrosion products). The latter can be serious because the transported crud eventually deposits in low velocity areas and can affect flow characteristics and component operations (such as valves). The crud also is activated as it passes through the neutron flux in the core and when it subsequently deposits in areas remote from the core, raises the radioactivity level in that area. This is a major problem in maintaining and repairing reactor components. Not only is the activity level high but cutting and welding operations produce airborne particles that might be ingested into the body.

The major corrosion problems associated with the operation of sodiumcooled reactors are somewhat different from those with water-cooled reactors. The same problems exist on the steam side, that is, pitting of steel components and chloride or caustic stress-corrosion cracking of stainless steel components. Sodium is a reactive metal and readily reacts with oxygen, nitrogen, and hydrogen and will pick up carbon. As the dissolved oxygen content in sodium increases, the corrosion rate of iron-base alloys also increases [10]. Nitrogen may cause nitriding under some conditions [11]. Hydrogen does not appear to be a problem because of its low content in sodium and the fact that most hydride-former metals (such as zirconium) react with the oxygen in the sodium to form a protective oxide surface layer [11]. (At temperatures >600 C, zirconium will dissolve its own oxide [11].) Carbon in sodium can lead to carburization of stainless steel [11,12]. In binary metallic systems, carbon may be transported from one material to the other. As an example, low-alloy steels in the cooler zone of a sodium circuit become decarburized while austenitic stainless steels in the hotter zone of the same circuit become carburized [13].

The removal and steam cleaning of components from a sodium system and their reinsertion into the sodium can be a potential problem if crevices or other areas of entrapment exist. When moisture contacts the sodium, sodium hydroxide is formed and hydrogen is evolved. On exposed surfaces, the NaOH is washed away or is slowly converted to Na₂CO₃ by reaction with CO₂ in the air. However, in crevices, the rate of formation of Na₂CO₃ is slow because of diffusion of CO₂. Thus, under these conditions, a component could be returned to the sodium coolant with NaOH in the crevice. If there are high stresses in this area, cracking can occur because studies have shown that NaOH or NaOH/Na will produce cracking in stressed stainless steel at temperatures on the order of 450 C [14–16]. For this reason, care must be exercised that moisture not enter a vessel that has been drained of sodium and is subsequently to be refilled with sodium and heated to high temperature.

The slow leakage of sodium into the atmosphere can also produce intergranular attack of stainless steel at ambient temperature [15]. Presumably Na_2O is the corrodent because concentrated NaOH and Na_2CO_3 are routinely handled in steel or stainless steel at ambient temperature with no corrosion problems.

A water-steam jet into sodium (as at a leak in a heat exchanger) produces rapid metal wastage of steel, stainless steel, and nickel-base alloys [17]. However, this is not a normal operating problem in sodium-cooled reactors.

Application of Standards

The standards that apply directly or indirectly to materials in, and the operation of, nuclear power plants are presented in Table 1. Related standards will be mentioned in the text and in the references at the end of the chapter. Except where stated, the standards apply to both water-cooled and sodium-cooled reactors. In the following sections, only the general features of the standards are discussed and for the detailed procedures one must consult the standard itself.

Material Requirements

Standards on corrosion criteria for steel, stainless steel, and nickel-base alloy sheet, plate, tubing, and piping are included in MIL SPECS and RDT

	TABLE 1-	-Standards and specifications relating to corrosion in the nuclear power industry.
Standard Number	Date	Title
SA-1 55	1970 ^a	American Society of Mechanical Engineers Specification for Electric-Fusion Welded Steel Pipe for High Temperature Service
SA-240	1968"	Specification for Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Fusion-
SA-312	1968"	Welded Untired Pressure Vessels Snecification for Seamless and Welded Austenitic Stainless Steel Pine
SB-407	1968	Specification for Nickel-Iron-Chromium Alloy Seamless Pipe and Tube
SB-409	1968ª	Specification for Nickel-Iron-Chromium Alloy Plates, Sheet, and Strip
		American Society for Testing and Materials
ASTM A 155-71	1971	Specification for Electric-Fusion Welded Steel Pipe for High-Pressure Service
ASTM A 240–71	1971	Specification for Stainless and Heat-Resisting Chromium and Chromium-Nickel Steel Plate, Sheet, and
		Strip for Fusion-Welded Unfired Pressure Vessels
ASTM A 312-71	1971	Specification for Seamless and Welded Austenitic Stainless Steel Pipe
ASTM A 262–70	1970	Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels
ASTM A 393-63	1963	Recommended Practice for Conducting Acidified Copper Sulfate Test for Intergranular Attack in Austenitic
I		Stainless Steel
ASTM B 407–71	1971	Specification for Nickel-Iron-Chromium Alloy Seamless Pipe and Tube
ASTM B 409–70	1970	Specification for Nickel-Iron-Chromium Alloy Plate, Sheet, and Strip
ASTM G 2–67	1967	Recommended Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys
ASTM G 28–71	1971	Method of Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich Chromium-Bearing Allovs
		National Association of Corrosion Engineers
NACE Standard TM-01-71	1971	Test Method Autoclave Corrosion Testing of Metals in High-Temperature Water
	U.S. A	tomic Energy Commission, Division of Reactor Development and Technology
RDT A1-1T	Oct. 1971	Coolant Composition in Pressurized Water Reactors
RDT A1-2 RDT A1-3	in prep. in prep.	Coolant Composition in Boiling Water Reactors Coolant Composition in Light Water Cooled Test, Research, and Experimental Reactors

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RDT A1-5	in prep.	Purity Specifications for Large Operating Sodium Systems
RDT C8-5T	Jan. 1972	Electrochemical Oxygen Meter for Sodium Service
RDT C8-6T	Jan. 1972	Hydrogen Meter for Sodium Service
RDT C8-7T	Jan. 1972	Diffusion Type Carbon Meter for Sodium Service
RDT C8-8	Jan. 1972	Equilibration Device for Measuring Nonmetallic Impurity Activities in Sodium
RDT E4-1T	Dec. 1971	Steam Generator for Pressurized Water Reactors
RDT E4-5T	Dec. 1970	Forced Circulation Cold Trap Assembly for Removal of Sodium Impurities
Amendment 1	Sept. 1971	
RDT E4-6T	April 1971	Intermediate Heat Exchanger for Liquid Metals
Amendment 1	June 1971	
RDT E4-7T	June 1971	Sodium to Air Heat Exchanger
Amendment 1	Oct. 1971	
RDT E4-17T	July 1971	Heat Exchanger, Class 2, Water-to-Water, Straight or U-Tube
RDT E5-1T	Dec. 1970	Pressurizer for Pressurized Water Reactors
RDT E8-16	to be prepared	Environmental Conditioning Stations for Refueling Operations
RDT E13-15T	July 1971	Fuel Assemblies for Pressurized Water Reactors
RDT E15-2T	July 1971	Requirements for Nuclear Components
Amendment 1	July 1971	
RDT F3-6T	July 1971	Nondestructive Examination
RDT F5-1T	March 1969	Cleaning and Cleanliness Requirements for Nuclear Reactor Components
RDT F5-4	to be prepared	Cleaning Components Contaminated with Sodium (Nonradioactive)
RDT F7-2T	Feb. 1969	Preparations for Sealing, Packaging, Packing, and Marking Components for Shipment and Storage
Amendment 1	Oct. 1971	
RDT M3-6T	May 1969	Austentitic Stainless Steel Pipe
RDT M3-9T	July 1971	Nickel-Iron-Chromium Alloy Seamless Pipe and Tubing
RDT M3-11T	July 1971	Carbon and Low Alloy Steel Welded Pipe
RDT M5-1T	July 1971	Stainless Steel Plate, Sheet, and Strip
RDT M5-7T	July 1971	Nickel-Iron-Chromium Alloys Plate, Sheet, and Strip
RDT M12-1T	Feb. 1969	Test Requirements for Thermal Insulating Materials for Use on Austenitic Stainless Steels
RDT M13-1T	June 1970	Reactor Grade Sodium-Purchase Specifications
Amendment 1	Oct. 1971	
Amendment 2	Dec. 1971	

Standard Number	Date	Title
	-	U.S. Government Federal and Military Specifications and Standards
Fed. Spec. QQ-P-35a	20 June 1968	Passivation Treatments for Austenitic, Ferritic, and Martensite Corrosion-Resisting Steel (Fastening Devices)
Federal Test Method STD No. 151a	6 May 1959	Intergranular-Corrosion Test for Corrosion Resistant Austenitic Steels
Method 021.1 NAVSHIPS 250-1500-1 Advance Change Notice No. 2	Jan. 1968 [.]	Standard for Welding of Reactor Coolant and Associated Systems and Components for Naval Nuclear Power Plants (Pressurized Water-Cooled Systems)
MIL-B-3196A	20 Feb. 1967 10 Lune 1966	Boilers and Related Equipment, Packaging of Military Snecification Steel Plate Sheet and Strin: Corrosion Resistant
MIL-T-23226A	26 Oct. 1964	Military Specification. Tube and Pipe, Corrosion-Resistant Steel, Seamless
^a ASME Boiler and P	ressure Vessel C	Ode Section II, 1968, Material Specs, Part A, Ferrous, and Winter and Summer, 1970 Addenda.

Standards. Included in the MIL SPECS are MIL-S-23196A (SHIPS) and MIL-T-23226A (SHIPS) for corrosion-resistant steel sheet and strip and tube and pipe. The standards require that the material be free of grain boundary carbide precipitates which can cause intergranular corrosion. (It should be noted that the operating temperature of some components in a sodium-cooled reactor may be in excess of 540 C and this temperature is sufficiently high to cause carbide precipitation at grain boundaries in austenitic stainless steels.) A hot-acid-etch test is specified according to Method 321 of FED-STD-151. This test consists of a 48-h exposure of the subject material to a boiling solution of 100 g of copper sulfate (CuSO₄·5H₂O) and 100 ml of sulfuric acid (H₂SO₄, sp gr 1.84) and sufficient distilled water to make 1000 ml of solution. Upon completion of the 48-h exposure, the specimens are bent and examined for cracks and fissures that are indications of intergranular attack. Flat specimens are bent through 180-deg over a diameter equal to the thickness (1T) of the specimen. Tube specimens are flattened as prescribed in ASTM A 370 [18]. However, FED-STD-151 has recently been modified and Method 321 now is identical with ASTM 393. The latter test contains the same provisons as those in Method 321 except that the exposure period in the boiling copper-sulfatesulfuric acid is 72 h instead of 48 h. As an interesting side light, there is increasing evidence that the copper sulfate-sulfuric acid test is "too mild" and does not detect many cases of sensitization and in particular, where the time at temperature is short and the carbon content of the stainless steel is low (0.04 to 0.05 percent). Research performed on the problem has revealed that the test can be made more sensitive by contacting the specimen with metallic copper during its exposure to the copper sulfate-sulfuric acid solution [19-22]. Accordingly, ASTM A 262 has recently been changed and now includes the copper-copper sulfate-sulfuric acid test. The procedures are essentially he same as those described in ASTM A 393 and Method 321 of FED-STD-151 except that the specimen is covered with copper shot or turnings and the exposure time is 24 h.

There are also standards for detecting susceptibility to intergranular attack in nickel-base alloys. ASTM G 28 specifies exposure to a boiling solution of 25-g reagent grade ferric sulfate $[Fe_2(SO_4)_3]$ and 236 ml reagent grade 95 to 98 percent sulfuric acid (H₂SO₄) added to 400 ml distilled water.

Alloy	Testing Time, h
Hastelloy Alloy C	24
Hastelloy Alloy C-276	24
Hastelloy Alloy G	120
Carpenter Stainless No. 20 Cb-3	120
Inconel Alloy 600	24
Incoloy Alloy 800	120
Incoloy Alloy 825	120

The presence of intergranular attack is usually determined by comparing the calculated corrosion rate to that for properly annealed material. Metallographic examination may also be used to determine the degree of intergranular attack.

The RDT standards pertaining to materials include RDT's M3-11T, M5-1T, M3-6T, M5-7T, and M3-9T. These are not complete standards but are additional requirements to ASME SA-155, SA-240, SA-312, SB-409, and SB-407, respectively, which, in turn, are identical with ASTM A 155, A 240, A 312, B 409, and B 407 respectively. The ASTM and ASME standards specify that stainless steel shall be heat treated to meet the mechanical property requirements of the specification and be capable of meeting the test for resistance to intergranular corrosion (ASTM A 393). However, the intergranular corrosion test is not required unless it is specified on the purchase order. No intergranular test is required for the nickel-iron-chromium alloys although the specified heat treatments are as hot-finished, annealed, or solution-annealed.

From a corrosion standpoint, the principal additional requirements in the RDT's specify cleanliness and the limits for chloride and sulfur contamination in handling stainless steel. The contamination requirements include: (1) Marking materials shall not contain sulfur, chlorine, or other halogens in amounts greater than 200 ppm; (2) All processing compounds, degreasing agents, cleaning solutions, and foreign materials shall be completely removed at any stage of processing prior to any elevated-temperature treatment; and (3) Any pickling or descaling in a bath containing chlorides shall be followed immediately by a nitric acid pickle, followed by immediate rinsing with hot water containing not more than 20 ppm chloride.

The above three procedures are designed to minimize the threat of stresscorrosion cracking of sensitized stainless steel and in the case of Item 2, the cracking of solution-treated material.

Manufacturing Requirements

Corrosion-related standards that pertain to manufacturing procedures are included in RDT Standards F5-1T, E4-6T, E4-7T, E4-17T, ES-1T, and E13-15T. The first of these deals with cleaning requirements and contains the following pertinent requirements:

1. Grades of water (A, B, or C) to be used in hydrostatic testing and rinsing of components.

2. Precautions against the use of oxidizing agents such as nitric acid or the exposure to halide-bearing environments such as salt air of stainless steels that have been sensitized by heating in the range 425 to 870 C.

3. Prohibition of the following where crevices are present (may be used if there are no crevices):

a. Vapor degreasing

b. Trisodium-phosphate degreasing

c. Acid cleaning

4. Prohibition of halogenated cleaning agents and solvents on austenitic stainless steels.

5. Prohibition of the use of materials containing lead or sulfur on nickel-base alloys (to prevent embrittlement if the component should be subsequently heated to high temperatures).

6. Prohibition of aluminum in contact with stainless steel or nickel-base alloys or zinc in contact with stainless steel.

7. Prohibition of mercury or mercury compounds in any equipment.

8. Prohibition of corrosion inhibitors from materials intended for coolant surfaces. This restriction is probably related to a case of intergranular pitting of heat-exchanger tubes where one of the proposed causes of the attack was the degradation of an inhibitor.

9. Clean room or clean area requirements starting with that stage of fabrication where critical surfaces that will be exposed to reactor coolant will no longer be accessible for cleaning or inspection.

10. The removal of rust from critical surfaces that will be exposed to reactor coolants. Rust contains ferric ions, frequently retains the corrodent (such as chlorides), and may be hygroscopic so that failure to remove rust could result in localized attack and possibly stress-corrosion cracking if the component is highly stressed.

11. Protection of components and materials from the general shop atmosphere or other contaminated atmospheres, such as salt air or blowing dust, where possible during fabrication and storage.

Surface finish and cleaning are specified in RDT E4-17T, E5-1T, and E13-15T. The latter repeats many of the restrictions described above and prohibits mercury, lead, phosphorus, zinc, cadmium, tin, antimony, bismuth, mischmetal, and other similar alloys during fabrication, cleaning, testing, or final assembly of components. RDT E5-1T prohibits electroplating on surfaces in contact with pressurized water or steam presumably because under certain conditions, electroplates, such as nickel corrode and spall and are transported by suspension or solution.

Federal Specification QQ-P-35 is often followed to passivate stainless steel after fabrication. The passivation treatment consists of immersion for 10 to 30 min at 70 to 155 F (depending upon the alloy) in a 20 to 25 volume percent nitric acid (HNO₃ at sp gr 1.42) solution containing 2 to 3 weight percent sodium dichromate (Na₂Cr₂O₇·2H₂O). An alternate procedure is 30 to 60 min in 20 to 50 volume percent HNO₃ (sp gr 1.42) at room temperature. This is followed by a hot-water rinse, and for ferritic or martensitic stainless steels, a 30-min immersion in 4 to 6 weight percent Na₂Cr₂O₇·2H₂O at 140 to 160 F followed by a hot-water rinse. A passivated surface must pass a 24-h exposure to 100 percent humidity at 100 F as prescribed in Method 101 of MIL STD 753 [23]. Many believe that the function of the passivation treatment is not to form a protective film but to remove contamination (particularly iron) from the surface and thereby prevent the localized breakdown of the already existing protective film during subsequent service.

Included in RDT E4-6T and E4-7T are requirements that crevices be minimized and corrosion allowances be included for liquid metal components. The corrosion allowance is to compensate for loss of material due to erosion, corrosion, carbon transport, sodium-water reaction effects and other surface wastage effects. The crevices are minimized to avoid retention of Na₂O or NaOH that might form if the component is removed from service, exposed to moist conditions, and then put back in service.

Packaging Transportation and Storage Requirements

The cleanliness and contamination requirements described in the previous two sections also apply to packaging, transportation, and storage. These are reiterated in RDT F7-2T plus additional prohibitions on materials containing fluorides and copper. (The intergranular attack of sensitized stainless steel by fluorides has been covered in the Discussion section.) Vaporphase inhibitors are also prohibited.

Carbon steel components may rust during shipment and storage. RDT F7-2T specifies that small carbon steel components (and other materials that do not resist atmospheric corrosion) be packaged in moisture-vapor proof envelopes that have been purged with a dry, inert gas such as nitrogen, argon, or helium free of dirt, dust, oil, or halogens, and with a dewpoint of -40 F or lower. A bagged desiccant that is nondeliquescent, nondusting, nonhalogenated, and chemically inert is to be inserted in the envelope. For large steel components, all openings are to be plugged and sealed with approved materials, the vessel is to be purged with dry, inert gas (see above) in a prescribed manner, a desiccant is to be inserted in the vessel, and a humidity card is to be included near a clear plastic (nonhalogenated) cap so that it can be monitored without admitting air to the unit. The amount of desiccant per total internal volume is specified.

RDT E4-1T specifies that a desiccant and humidity chart shall be placed on the steam side of all steam generators.

MIL-B-3180B describes the packaging of the waterside of boilers which is pertinent to surfaces that do not come in contact with the nuclear-reactor coolant. The waterside is drained and dried and is entirely coated with a preservative that, when applied to steel, must be capable of passing a 30-day humidity test and a 6-month outdoor storage in a louvered shed as described in ASTM 1748 [24]. All openings are then sealed with tape, plastic caps, or barrier material depending on their size. To put the unit back in operation, it is cleaned with a detergent conforming to MIL-D-16791 Type I [25] and then rinsed.

Prior to putting carbon steel boilers into operation, they are frequently acid cleaned with acetic acid or inhibited HCl [26] and are then boiled out

with a passivator solution to build up a protective film. MIL-P-24138 (SHIPS) [27] specifies the composition of the dry passivator compound for Navy boilers to be 50 weight percent sodium nitrite (NaNO₂), 25 weight percent sodium dihydrogen phosphate (NaH₂PO₄), and 25 weight percent disodium monohydrogen phosphate (Na₂HPO₄).

On-Site Erection Requirements

There appear to be no standards that relate directly to the on-site erection of reactors. However, conscientious contractors would abide by the cleanliness and contamination requirements described in the preceding sections. Of particular importance on-site are the exclusion from sensitized stainless steel of marine air and weld fumes and spatter from coated electrodes because the attendant chlorides and fluorides can cause intergranular attack or stress-corrosion cracking.

Of particular importance in reactor-plant erection is the type of insulation used on heated stainless steel pipes and vessels. Mineral-base thermal insulation materials, cements, and adhesives can contain leachable chlorides. If water drips onto the insulation, these chlorides can be carried to the hot surface below and cause stress-corrosion cracking of the stainless steel component. Thus, low chloride insulation materials are specified. In the event that the water dripping onto the insulation may itself contain chlorides, some mineral insulation materials are treated with sodium silicate that affords some inhibition to stress corrosion.

RDT M12-1T specifies a corrosion test that a mineral insulation must pass if it is to be used on austentic stainless steel. The test consists of attaching four sensitized Type 304 U-bend specimens snugly onto an Inconel pipe so that the compression side of the U-bend contacts the surface of the pipe. (See Fig. 1.) The insulation is then fit snugly onto the tension side of the U-bends and is placed in a stainless steel container so that the portion of the insulation but not the U-bends will be immersed when the container is filled with distilled water. The interior of the pipe is heated so that the water wicking up through the insulation evaporates on the hot specimens. The test period is 28 days of continuous exposure at a prescribed rate of evaporation of water. Upon completion of the test, the specimens are cleaned and examined at a magnification of 30 for evidence of cracking at the U-bend or below the bolt holes. The insulation is considered rejectable if two or more of the four specimens contain cracks.

The acceptance criteria for the above test is open to question in view of the small sample size and the known erratic failure pattern of stress-corrosion samples. In the usual tests for stress corrosion, if one of four specimens exhibits cracking in a finite exposure period, then the conditions would generally be considered to be conducive to initiating stress-corrosion cracking.



FIG. 1—Schematic diagram of apparatus for conducting the wet insulation test (as reproduced from RDT M12-1T).

Reactor Operation

Water-Cooled Reactors

Coolant Compositions-RDT Standard A1-1T specifies the coolant composition in pressurized-water reactors and mentions that materials in contact with the primary coolant may include austenitic stainless steels, nickel-chromium-iron alloys (such as Inconel 600), and Zircaloy 2 or Zircaloy 4. The make-up water quality before chemical additions is to be pH 6.0 to 8.0 (25 C), specific conductivity 1.0 µmhos/cm max. (25 C), chloride 0.15 ppm max., fluoride, 0.10 ppm max., and total suspended solids 1.0 ppm max. For neutral reactor coolants the water should meet the above specifications except that the allowable specific conductivity is 5.0 μ mhos/cm (max), dissolved hydrogen should be 10 cc (STP)/kg H₂O min (15 to 60 cc/kg normal), and dissolved oxygen should be 0.10 ppm max. The hydrogen is added to promote radiolytic recombination with oxygen. A low oxygen level is desired to minimize the amount of crud (corrosion products) that are released to the system. Hydrogen also prevents the formation of nitric acid which occurs under nuclear radiation when oxygen and nitrogen are present in the coolant. pH control may be used to minimize the formation, transport, and deposition of crud. In the absence of boric acid, the following concentrations of alkaline agents are recommended:

Ammonium hydroxide (NH₄OH) 10 to 40 ppm NH₃, pH 9.9 to 10.3 (25 C) Lithium hydroxide (LiOH) 0.2 to 2.2 ppm Li, pH 9.5 to 10.5 (25 C) Potassium hydroxide (KOH) 1 to 12 ppm K, pH 9.5 to 10.5 (25 C) LiOH and KOH should be avoided in systems containing heated crevices or undrainable stagnant spaces where the additives could concentrate and cause localized corrosion (such as pitting or stress-corrosion cracking). No chemical additive should contain more than 30-ppm halide in its most concentrated commercially available form. Specifications are also given for reactor coolants that use boric acid for reactivity control either with or without alkaline (NH₄OH, LiOH, or KOH) additions for pH control.

RDT standards are being prepared but have not yet been issued for coolant compositions of boiling-water reactors (RDT A1-2) and of light water test, research, and experimental reactors (RDT A1-3).

Testing Methods—ASTM G 2 and NACE TM-01-71 specify test methods for evaluating materials in water-cooled reactor environments. The former deals with the testing of zirconium alloys in 360 C water and 399 C steam



FIG. 2—Photograph of principal autoclave components. Left to right: main closure nut, autoclave head and corrosion coupons, autoclave body, and gasket.

while the latter deals with structural and containment materials (primarily stainless steels, nickel-base alloys, and steels). NACE is currently (1972) balloting on a standard for dynamic corrosion testing in water. ASTM B 356 [28] contains a brief description of the 399 C-1500 psi steam test for zirconium and zirconium alloys which is now covered in greater detail in ASTM G 2.

Examples of the types of set ups used in these tests are shown in Figs. 2 and 3. Many variables must be considered in testing samples in simulated water-reactor coolants and these are discussed in detail in Ref 9. Many of these variables have been considered in ASTM G 2 and NACE TM-01-71. For example ASTM G 2 requires that all new or reworked autoclave components be subjected to 399 C-1500 psi steam for at least 1 day to oxidize the parts and insure that the autoclave is clean. To meet the latter requirement, water of initial specific resistivity of 500,000 ohm-cm shall be at least 100,000 ohm-cm after test. Oxidizing the surfaces minimizes galvanic effects, and under most conditions bare specimens can be supported on preoxidized hooks with no adverse galvanic effects. The procedures for preparing the zirconium alloy surfaces are carefully outlined to prevent retention of the HNO₃-HF pickling solution on the specimen surface and subsequent accelerated corrosion when exposed to the hightemperature water. ASTM G 2 also specifies a noncorrosion-resistant control coupon for the 399 C-1500 psi steam test because experience has shown that steam from water containing small quantities (to 6 ppm) of



FIG. 3—Schematic diagram of dynamic corrosion loop.

calcium, chloride, or sodium ions has an inhibiting effect on the corrosion of Zircaloy [9,29]. On the other hand, 0.12 to 1.3 ppm silicon in the water will cause accelerated attack of Zircaloy in the steam test depending on the heat treatment of the Zircaloy [30].

In the above tests, the zirconium alloys are evaluated on weight gain and appearance. Good quality material should exhibit a lustrous black film after test. Within segments of the industry, reference sets of panels are used to evaluate the appearance of the specimens. NACE TM-01-71 specifies that the specimens are to be descaled by procedures described in NACE Publication 7D167 [31]. ASTM G 1 [32] also describes one of the electrolytic methods that is used extensively to descale corrosion test coupons.

Inspection Methods-Inspection of the primary water side of reactor components for evidence of corrosion is often required where corrosion has occurred or is suspected (as in the possibility of stress-corrosion cracking of sensitized stainless steel). This inspection is most frequently accomplished with dye penetrant because of its simplicity and ease of handling. The requirements for nondestructive testing by this technique are presented in RDT F3-6T, RDT E15-2T, and NAVSHIPS 250-1500-1. Among other things, the RDT standards describe the size, type, and distribution of acceptable and unacceptable defects as well as a maximum allowable halogen or sulfur level in the cleaner, penetrant, or developer of 0.5 percent. NAVSHIPS 250-1500-1 allows a maximum of 1 percent halogens or sulfur. These tolerances appear to be too liberal when it is considered that they represent concentration levels of 5000 to 10,000 ppm and the amount of chloride in a chloride stress-corrosion crack in stainless steel is often on the order of several thousand ppm. Thus, retention of the penetrant in a crack or crevice might lead to additional cracking because of the retained chloride ion. Sulfur would not be expected to be a problem with stainless steel, but might conceivably cause problems with nickel-base alloys.

MIL-STD-271D(SHIPS) and MIL-I-23135C(ASG) also describe penetrant inspection methods [33,34]. They are not nuclear oriented, apply to many alloy systems, and do not limit halogens or sulfur in the cleaner, penetrant, or developer and in fact, MIL-STD-271D permits the use of trichloroethylene and perchloroethylene to clean components prior to inspection.

Sodium-Cooled Reactors

Sodium Composition—RDT M13-1T specifies that sodium purchased for use in liquid metal fast breeder reactors shall have a minimum sodium content of 99.9 weight percent as determined by total alkalinity. In nonradioactive environments, the allowable sodium impurities are:

calcium	10 ppm
carbon	30 ppm
potassium	1000 ppm
halogens	50 ppm

The same limits apply for radioactive environments plus the additional limits listed below.

boron	5 ppm
cadmium	2 ppm
indium	10 ppm
lithium	5 ppm
silver	5 ppm
sulfur	15 ppm

One of the main contributors to corrosion, oxygen, is not specified. Presumably, the oxygen content is expected to be reduced by cold trapping or hot trapping during the initial stages of plant shakedown operations. RDT M13-1T also specifies that equipment used in contact with sodium shall be free of rust, dirt, oil, moisture or other material that might contaminate the sodium. Rust will be reduced by sodium with a resultant increase in the oxygen content and probably the hydrogen content of the sodium. Dirt and oil can lead to carbon pickup and an increase in carburizing potential of the sodium. Moisture can lead to oxygen and hydrogen pickup or the formation of sodium hydroxide with attendant increases in the corrosivity of the sodium.

Operating Conditions—RDT E4-7T specifies that the use of steels in sodium shall be based on the mechanical properties, metallurgical stability, and sodium compatibility required for the sodium system at design temperatures. In general, carbon steels are limited to <370 C, chromium-molybdenum steels ($2\frac{1}{2}$ Cr-1Mo, 5Cr- $\frac{1}{2}$ Mo, 9Cr-1Mo) are limited to 540 C, and the austenitic stainless steels may be used at higher temperatures.

RDT 4-5T describes the requirements for a forced circulation coldtrap assembly for the removal of sodium impurities. These are essential to reactor operation to maintain low levels of impurities particularly oxygen and carbon, which can lead to corrosion and carburization of components. RDT Standards C8-5T, C8-6T, C8-7T, and C8-8T deal with meters or devices for measuring oxygen, hydrogen, carbon, and nonmetallic impurity activities in sodium. These standards describe the limits that the meter will detect, but do not specify the minimum acceptable levels for these impurities.

ANL/ST-6 describes analytical techniques for measuring metallic and nonmetallic impurities in sodium [35]. The range of detection of the non-metallic impurities by these techniques are:

Impurity	Detection Range, p	pm Accuracy
Oxygen		
Total Consumption	3 to 100	± 30 percent
Extrusion Method	<5	±1 ppm
Vanadium Wire	0.1 to 14	± 10 percent
Hydrogen	0.5 to 25	± 10 percent at 0.5 to 5.0 ppm
Carbon	0.5 to 1000	0.5 ppm at 0.5 to 10 ppm

Nitrogen	0.1 to 100	± 15 percent at 0.5 to 10 ppm
Chlorine	Limit is 0.5	± 10 to 15 percent at 5 ppm

RDT E8-16 and F5-4 have been designated for environmental conditioning during refueling operations and for cleaning sodium components, but the preparation of these standards has not yet been started. They are expected to contain provisions that will take into account the corrosive environments (Na₂O and NaOH) that can be produced when moisture contacts sodium.

RDT A1-5 on purity specifications for large operating sodium systems has been prepared and is being revised, but has not yet been issued.

Inspection—Liquid penetrant inspection is also used extensively on components in sodium service (see RDT E4-5T, E4-6T, E4-7T). The halide limitation (described under Inspection-Water-Cooled Reactors) also applies to sodium-cooled reactors particularly on steam surfaces and external surfaces that are exposed to ambient air during shutdown. The sulfur limitations are particularly pertinent to sodium service if nickel alloys are used in the high temperature portion of the system, because sulfur embrittlement is a potential problem.

Areas Requiring Additional Attention

Although the nuclear power industry is still in its early stages of growth, major strides have been made in providing corrosion standards to guide its operation. As to be expected, there are still some gaps that have not yet been filled. In particular, attention should be given to on-site plant erection practices. Of major importance is the protection of both primary and external surfaces of stainless steels from construction debris and dirt, marine atmosphere, and welding fumes. These can lead to intergranular attack or stress-corrosion cracking under the conditions described in the background section.

As more reactors are placed in operation, repair and inspection practices will require standardization. In particular, are the problems of reducing the radiation levels in the vicinity of the repair site and the further reduction of the allowable halides in the liquid penetrants used in inspections.

In sodium technology, the principal problem appears to be a standard means for assuring that steam cleaning or other moisture contact on sodium covered component will not result in the retention of NaOH or Na₂O that can lead to localized attack when the component is reintroduced to hot sodium. Perhaps, the introduction of CO_2 during these operations could be used to form sodium carbonate which is less corrosive.

In water-cooled reactors, the principal corrosion problem areas requiring attention continue to be transported corrosion products (crud) and sensitized stainless steels. Significant success with crud has been attained by pH control in pressurized-water reactors. However, it would appear that eventually the water-cooled reactors will have to be descaled to reduce the crud inventories and standards will be needed to avoid corrosion problems. The sensitization problem is now receiving attention. Yet to be resolved are what degrees of sensitization are harmful and what simple tests can be applied to detect these degrees of sensitization.

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Chapter 9

Corrosion Standards and Control in the Chemical Industry

L. W. $Gleekman^1$

The chemical engineer in the chemical industry, responsible for the selection of materials of construction, currently must be more than a corrosion engineer; he must be in the broadest sense a materials engineer. In view of the fact that materials other than metals are widely used in the chemical industry, this engineer must know more than the metallurgy and electrochemistry of the destruction of metals (commonly called corrosion). He must know the technical and scientific information with regard to the deterioration of plastics, graphite, wood, rubber, concrete, roofing materials, coatings, glass, brick, mortars, among many materials.

By chemical industry is not meant that segment of business uniquely concerned with the production and manufacture of chemicals. It is but an extension of chemical engineering when one considers that the fertilizer industry, the pulp and paper industry, the petroleum refinery, the mining and metal extraction, the petrochemical industry-all these are variations of the chemical industry. It is interesting to speculate what these industries have in common and thus to establish why corrosion control in these industries is basically similar. Such similarities include the handling of liquids, solids, and gases, separately and in combination. There is also the handling and/or production of acids, bases, and salts, both inorganic and organic. There are power requirements for the transmission and movement of process fluids as well as for the generation of heat to increase the rate of many of the chemical reactions. There is a need, in most cases in the industries mentioned, for purity of product which is one aspect of no, or low, corrosion. As with all industry, there is a need for raw materials and, of course, an outlet for the finished materials as well as control of waste or by-products. The present day economy demands maximum life of processing equipment at minimum cost, with minimum labor requirements both in the operation of the plant to produce the chemicals and in the maintenance of the plant.

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These various factors have had a major influence on the materials of construction used in these industries and, indeed, on the philosophy of the selection of these materials of construction. In the early days of the chemical industry, before the development of joining techniques such as welding and brazing and before the development of what is now commonly called corrosion-resistant alloys, the materials then used were those which were readily available either naturally, or within the production techniques of the then existing industries. For example, wood was (and still is to a lesser degree) a widely used material of construction for vessels, tanks, and pipes. Natural rubber in sheet form was also an extensively utilized material. Of the metals, cast iron was perhaps the most widely used early metallic substance because of its low cost, relative ease of formation (low melting point and tolerance for impurities), and fair strength in compression. Copper and brass and bronze were used where their special properties, such as heat transfer or rotating load-carrying capacity, as in bearings, could be justified. All these early materials had their limitations, and it is hard to say whether the limitations of the materials brought on the development of new competing materials, or whether the competing materials would have developed in and of themselves, irrespective of the limitations of the early materials.

The intricacies and size of equipment in the early chemical industry, the absence of refinements in process controls, inexpensive labor, and readily available land for plant sites, were among factors which led to the extensive use of cast iron. It was the common situation, at least in the chlor-alkali phase of the chemical industry, for virtually every major manufacturing company or plant to have its own foundry. In the early days of the industry, not only were there no standards in corrosion testing, but standards were lacking for dimensional values on pumps, valves, flanges, etc. For such reasons, each company developed their own internal standards in manufacturing their process equipment; this was in preference to farming out the work to jobbing foundries. It was not uncommon, within so short a period as the early 1960s, to find certain chemical companies producing cast iron caustic fusion pots in which 73 percent caustic soda was concentrated to close to 100 percent. These pots were approximately 10 ft in diameter and weighed 10 tons with an approximate 1-in. wall thickness. It should also be pointed out that in the early days of the chemical industry, as was virtually true in every industry, each company had what it felt were certain manufacturing and processing secrets which they did not want to divulge to their competitors. These included design details of the equipment. For this reason, it was then justifiable in the eyes of the engineers involved to manufacture this equipment within the confines of the company rather than to have it manufactured by a concern whose shop was open to chemical competitors. In a soda ash plant, it is common today to see the carbonating towers and the still units, both of which are large in diameter and quite tall (up to 9 to 12 ft in diameter and 100 ft tall) made from cast iron sections.

This is true not only for the older plants but even for plants built in 1950. Part of this may be due to the desire for interchangeability of new equipment with old, but the fact remains that in this segment of the chemical process industry, cast iron is still a strong contender in spite of the proven corrosion resistance, lesser wall thickness, and improved ease of fabrication of such materials as aluminum, stainless steel, and titanium.

It is interesting to note that the older industries fabricating the materials previously mentioned, (cast iron, wood, rubber, and glass) not only have not disappeared from the scene, but are trying to recoup the losses which they had made to the newer competing materials. A well qualified materials engineer today will not merely specify "cast iron": he will specify "materials to be ASTM A 48-64 Class 20." Here he indicates the strength of the cast iron to be used, or he may indicate the alloying elements to be added to the cast iron to give it a particular corrosion resistance in a given environment. This is but one phase of the revitalization of cast iron as a material of construction in the chemical process industry.

Fabricators of wood equipment have formed an organization known as the Wood Institute where presumably they pool certain experiences and developments to further the use of their materials in other using industries. Certain large size applications such as storage tanks still continue to be made in wood in certain industries. Because of the improvements that have occurred in wood technology, such as impregnation of wood with chemically resistant resins (phenolic and furane in particular), the impregnated material offers many corrosion advantages that cannot be achieved with unimpregnated wood. While natural rubber, in many cases, has given way to synthetic elastomers which have better life and improved oxidization and temperature resistance, nonetheless, natural rubber is still considered a standard elastomeric material of construction usually as a lining rather than a self-supporting material. Glass, of course, has been the favored material for use by chemists since perhaps the early work of the alchemists in the Middle Ages; while it has size limitations and also a fragility factor, it is used quite extensively for certain shapes, such as cylinders, in the form of pipe, etc. As will be seen subsequently, techniques have been developed to overcome the fragility aspects of glass and also the limitations on joining.

Because of weight considerations, formability, and the resulting ability to fabricate a vessel that will have maximum through-put with minimum metal involved, wrought metals are more widely used in the chemical industry than cast metals or other materials. *Corrosion Data Survey*, published by the National Association of Corrosion Engineers, has information on the following classes of metals; iron-base, copper-base, nickel-base, aluminumbase, precious metals, reactive metals, and others. In each one of these categories, there is considerable variation in corrosion resistance and also in price. The question that the corrosion and materials engineer faces is what material to select for a given piece of equipment in a given process and how to know that the material he has selected will have the combination of properties including costs and long life desired.

Corrosion Testing

One comes then, to the matter of corrosion standards and control for process (immersion) conditions as opposed to what will be discussed subsequently, corrosion standards and control for atmospheric conditions. The early work on the procedures to systematically select materials of construction for process conditions was that done by the Research and Development Department of the International Nickel Company sometime prior to 1930. This led ultimately to the development of the INCO Corrosion Test Spool which, in spite of the several standards which have been written and adopted by both ASTM and NACE, in particular, is still popularly known by that name rather than by association standard number.² The reader who wishes more detailed information on this subject should go to the Edgar Marburg lecture of 1951 by Francis LaQue on "Corrosion Testing" [1].³ He will find there a discussion not only for process conditions but virtually every other aspect of corrosion testing. The popularity of the INCO Test Spool is seen by the fact that since the early 30s, approximately 6000 of these assemblies have been distributed by International Nickel Company to those interested in determining the corrosion rate of metals and alloys. The INCO Test Spool has served to revolutionize corrosion testing under process conditions, in more than several ways.

1. It took from the hands of the chemists who, in establishing process reactions in the early days, determined materials of construction other than laboratory glassware. The habit of the chemist from his training was that of expressing everything as a percent. Thus, early corrosion data may have indicated that Metal A had a 1 percent weight loss while Metal B had a 3-percent weight loss under presumably identical process conditions; therefore, Metal A was superior to Metal B.

2. The INCO Test Spool standardized the size and shape of test specimens; this facilitated calculating the area of the samples which was a necessary step in the determination of weight loss per unit area per unit time.

3. The INCO Test Spool standardized on the number of identical specimens to be exposed to achieve a consistent statistical value. Samples of a given metal in a given heat-treated condition were used. Usually only two identical samples were exposed to increase the total number of specimens of different materials exposed to the process environment.

4. The INCO Test Spool with its determination of weight loss per unit area per unit time as milligrams per square decimeter per day (mdd) led

² Recommended Practice for Conducting Plant Corrosion Tests, ASTM G 4–68; Laboratory Corrosion Testing of Metals for the Process Industries, NACE TM-01-69.

³ Italic numbers in brackets refer to references listed at end of this chapter.

directly into the concept of corrosion allowance, as so many inches per year of attack. This was achieved by the simple procedure of dividing mdd by density in consistent units and converting to the desired units of corrosion allowance.

5. The INCO Corrosion Test Spool tested other than the general corrosion rate based only on weight loss. The crevice between the spacers used to separate samples served for many alloys to indicate their susceptibility to crevice corrosion; the stamping used to identify the specimens by code served to indicate the susceptibility of certain metals and alloys to stress corrosion cracking. The size of the sample was ideal for heat treatment so that sensitization effects could be imparted to the sample to simulate various conditions of welding. If desired, welded specimens could be formed into the shape used on INCO Test Spools. Also, where desired, specimens could be coupled together to achieve galvanic effects that might inadvertently be encountered in service. About the only thing that the INCO Test Spool could not do was to subject the samples to differential velocity conditions on one test spool or to different conditions of heat transfer on the same test spool. However, two or more spools with the same samples could be subjected to different velocity or heat transfer conditions, and so partially bring forth the desired answer. In addition, the shape of the INCO Test Spool did not allow for testing under combined liquid and vapor conditions with measured weight loss for each condition. Floating supports for test spools were devised which suspended a test spool accurately at the interface so that half of the specimen was in the liquid and half in vapor. Here, however, one had to rely on measurement of thickness changes (before and after exposure) or the depth of pitting in each phase to come up with meaningful results. On the other hand, it was again fairly simple to use two INCO Test Spools, one in the liquid phase, and one in the vapor phase, and possibly even a third under condensing conditions from the vapor phase to get weight loss figures which could be quantitative for corrosion allowance, along with the measurement of pitting tendencies.

ASTM has through the years worked out standards and practices for corrosion testing. This currently manifests itself in Recommended Practice For Conducting Plant Corrosion Tests which has the designation G 4–68. This replaces Standard A 224–46, in itself an outgrowth of the INCO Test Spool. Among other things that Recommended Practice G 4 does is to indicate the data that can be derived from a test spool, most of which falls in with the above. One additional important consideration is that of metasomatic corrosion and its determination. This is the condition in which one constituent is selectively removed from an alloy in what used to be called by the most common phenomenon, dezincification. Metasomatic corrosion is generally not determined by weight loss but by bending the sample after the exposure period and checking the microstructure of the surface to determine the selective corrosion of one or more constituents.

The INCO Test Spool does not always appear in the form normally supplied by INCO and outlined in Recommended Practice G 4. Modifications of the test spool have been developed for use in pipes and inside tubes. Figure 1 shows a modified INCO Test Spool arranged for insertion and removal into a process vessel while the vessel is operating. The samples are mounted on a corrosion resistant rod which allows the samples to be withdrawn from the vessel through a gate valve into a chamber which withstands the process temperature and pressure conditions of the vessel. Thereafter, the gate valve is closed and the samples then can be removed without the necessity of a process shut-down of the unit. Oftentimes, samples are suspended on plastic cord such as Saran or Teflon woven braid. One fundamental aspect of this immersion or "dunk" corrosion testing, as it is often called by electrochemists, is that the samples must be retrievable at the end of the test. There is nothing more discouraging or embarrassing to a corrosion engineer than to find that the samples thought to be on the end of the test cord have disappeared because the cord holding the samples broke.

6. Part of the problem of standard specimen for weight loss corrosion data is the removal of any corrosion products on samples in a standard manner. Such corrosion products must be removed since generally they correspond to an increase in weight and thus, with corrosion rate being determined by weight loss per unit area, could be misleading. Again, ASTM has established Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens, G 1–67.



FIG. 1—Schematic drawing of modified INCO test spool arranged for use in an operating process vessel.

Stress Corrosion Testing

This is a complicated topic as seen by the fact that many symposia have been organized around this theme to bring together the procedures and experiences that those in the field have been following. While many fine test methods have been proposed, as of this writing there is no one standard adopted by any group for stress corrosion testing. The reason for this is due to the variety of stress modes to which metal can be subjected while undergoing corrosive conditions. The old adage, "there is no test like a service test," would certainly be applicable here if one could afford the time, the equipment and duplication of process conditions. Since this chapter is not uniquely devoted to stress corrosion testing, there will be no attempt made to synthesize in detail the developments which appear in the literature. Instead the reader is referred to Effect of Stress on Corrosion by Dr. J. F. Bates of the Applied Research Laboratory of U.S. Steel Corporation which, in addition to being a fine discussion, also contains an excellent bibliography [2]. Dr. Bates points out two widely used tests in the U.S. Steel organization for stress corrosion; the cup-and-circular-weld specimen and the tuning fork. The first uses the Ericksen cup tester (nominally used to measure the ductility and drawing characteristics of sheet materials) plus a weld using the same material as the sheet; the combination imposes mechanical and thermal stresses and metallurgical structural changes. In addition, stamped identification, punched and drilled holes, and sheared edges impose conditions similar to actual fabrication variables. The tuning-fork samples can have as many variables and, in addition, allow predetermined values of stress to be imposed.

Not all tests can be, or should be, service tests or simulated service tests. To bring about standard methodology in laboratory testing, NACE, through its Technical Practices Committee in 1969, issued Standard Test Method TM-01-69 on "Laboratory Corrosion Testing of Metals for the Process Industries." In this test method, the factors which influence laboratory tests were discussed. These factors include specimen preparation, apparatus, test conditions (solution composition, temperature, velocity, aeration, volume, method of supporting specimens, and duration of the tests), methods of cleaning specimens, evaluation of results and calculation of corrosion rates. Since this is a laboratory method, the techniques of handling the specimens are slightly different than those involved in plant corrosion test G 4. In this method, a so-called resin flask is used as the container with a reflux condenser to prevent the loss of corrodent by evaporation. Four specimens are exposed at one time in this test compared to the plant corrosion testing. This standard also includes a reprint of the planned interval test of Wachter and Treseder [3] with regard to determining the effect of exposure period on the corrosion of metals and also the effect of the corrosivity of the environment. This procedure does not require the removal of solid corrosion products between exposure periods. NACE has a unit committee, T-5E, working on stress corrosion cracking (SCC) of all metallic materials from austenitic stainless steel through, and including, aluminum and low alloy steels. So far as is known at the present time, there have been no standards on corrosion testing coming out of this committee, though liasion is maintained with ASTM, the Metals Properties Council, and others. This group is particularly interested in environmental effects in stress corrosion cracking. A similar group which is very active in this regard is ASTM Committee G 01.06. Section 1 of this Committee is investigating specimens such as C-rings, U-bends, bent-beams, and use of direct tension. Section 2 of this ASTM committee is concerned with testing environments and may be expected to produce a recommended practice shortly for stress corrosion tests for titanium alloys, for aluminum alloy 7039, and for certain copper base alloys.

Another fine reference for stress corrosion testing is the chapter "Corrosion Testing" by Dr. M. G. Fontana in the NACE, *Proceedings of the Short Course on Process Industry Corrosion*, Sept. 1960 [4]. This 400 plus page loose-bound book still is an excellent compendium on many aspects of chemical industry corrosion problems and solutions. It is regrettable that it never appeared in hard-cover form. However, Dr. Fontana's joint book with Dr. N. D. Greene, *Corrosion Engineering*, contains much of his work from his 1960 lecture plus much more, drawing, as it does, on his many productive years with the duPont Company and his years of teaching, research, and consulting at Ohio State University [5].

Accelerated Corrosion Testing

Experiences in the chemical industry have shown that accelerated corrosion tests are often misleading in comparison with the procedures outlined for the plant corrosion test and, as indicated above, for the laboratory corrosion test. As a result, relatively little emphasis in the chemical process industry, and its related adjuncts, is placed on accelerated tests. However, as a reference for those who may be interested in standards which may exist, four ASTM standards are listed below which give reliable results in accelerated corrosion testing for certain materials in certain simulated environments. These include:

B 117-64, Salt Spray (Fog) Testing

B 287-68, Acetic Acid-Salt Spray (Fog) Testing

B 368,-68, Copper-Accelerated Acetic Acid Salt Spray (Fog) Testing (CASS Test)

B 380-65, Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure

In this connection it is considered wise to quote, hopefully not out of context, the words of Francis LaQue, given at a talk many years ago to a

group of chemical industry and automotive industry engineers, when asked what he thought of the salt spray test, Mr. LaQue stated, "Materials that do well in the salt spray test should be used to build salt spray test cabinets!"

Galvanic Corrosion Testing

This was one of the earliest topics of corrosion to be investigated for the very simple reason that the corrosion behavior of two metals coupled together serves to explain in a theoretical way the behavior of parts of the same metal corroding at different rates. The concept of anodes and cathodes is most easily drawn by using one metal whose behavior in the electromotive force series or the galvanic series is known to be more active than a second metal to which it was coupled.

Again, it was the early work of LaQue of International Nickel Company who pointed out the importance of the relative size of the anode and cathode being coupled. It was not sufficient merely to put two pieces of metal in contact, irrespective of the size of the materials. One had to recognize, as was developed by the early work of LaQue, that a small anode coupled to a large cathode would corrode at an extremely high rate compared to a large anode coupled to a small cathode. All testing for galvanic effects in corrosion has to take into account the relative anodecathode size. In addition, the corrosion products from the anode must be considered in terms of the possibility they have in increasing the electrical resistance between the two specimens coupled together. It is for this reason in particular that the INCO Test Spool lends itself to the testing of galvanic corrosion behavior where the two specimens are placed in contact rather than being separated by plastic insulators. Where design conditions are such that galvanic coupling of dissimilar metals cannot be avoided, it is best in testing to simulate these design conditions to establish the relative corrosivity of the couple, taking into account size effects. LaQue discusses this with sketches of equipment in his Marburg Lecture [1].

Velocity Conditions on Corrosion

Early quantitative corrosion experimenters established what have become the standards for determining the effect of velocity on corrosion rate. Among these were Dr. Mars G. Fontana at Ohio State University whose writings on this go back to his early regular monthly publications on corrosion in *Industrial and Engineering Chemistry*, back in the late '40s and continuing into the '50s. Whitney and Fisher at Monsanto in St. Louis were also prominent in this work. In essence, velocity corrosion testing consists on having a pump drawing the corrosive medium from a reservoir and moving it through pipes which often serve as the corrosion specimen in a closed loop back to the reservoir. To simultaneously test the effect of the temperature, there is usually a source of heat input to the circuit. Oftentimes the test specimen is the equivalent of a one-tube heat exchanger or possibly a multi-tube heat exchanger where the inside diameter of the tubing governs the velocity of the process fluid in the test unit. Most of the data which is now available for the limiting velocity on corrosion in surface condensers, heat exchangers and other tubular heat transfer devices come from procedures of the sort mentioned. The Navy Department through the work of W. Lee Williams at the Naval Experimental Station in Annapolis deserves much credit for organizing the work and procedure along these lines.

Committee T-5A of the National Association of Corrosion Engineers, dealing with corrosion in the chemical industry, has for years attempted to standardize a procedure on velocity corrosion testing, first through a series of round-robin tests of process fluids in different apparatus, and subsequently through the development of an actual testing procedure. This is now manifesting itself in a test method which is in the final stages of publication by the corrosion engineers. In the meantime, NACE has developed Standard Test Method TM-02-70, Method of Conducting Controlled Velocity Laboratory Corrosion Tests. In this standard, a corrosive solution is moved at a known tangential velocity across the face of one or more corrosion test specimens. Velocities of 8 ft/s or 15 ft/s are obtainable depending on the agitator drive used. This work derives in major part from the original work of R. J. Landrum of duPont and may be found in U.S. Patent 3,228,236 (1969). Landrum's paper, "Evaluation of Structural Materials for Corrosion Resistance," not only contains an outstanding discussion of corrosion testing in general but velocity corrosion testing in particular [6].

Figure 2 shows a laboratory velocity tester used to simulate expected conditions in a chemical plant. As indicated earlier, this consists of a reservoir from which the process fluid is drawn by a pump, sent through a heat exchanger and then through a series of pipes whose corrosion resistance is to be evaluated. The writer made use of this technique in a pilot plant for a chemical company about to build a large size unit. The circulating tester simulated the velocity conditions expected to be encountered in the main plant, testing a series of reinforced plastic pipes as well as several different metallic pipes. Evaluation was carried out by sectioning the pipes longitudinally at the end of the test and determining the loss in thickness for the plastic pipes and metallurgical changes such as the metasomatic corrosion of the metallic specimens. For a test of this sort to be meaningful, the material that has the best corrosion resistance must also have good fabricating capabilities. In the case of plastic pipes, this means the ability to attach flanges and to have fittings and valves available in the same material with proven corrosion resistance of all components. Thus, if the pipe is filament wound and the flange press-molded, the flange and its adhesive must withstand the corrodents equally well with the pipe proper.

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(a)



(b)

FIG. 2—Photographs of corrosion test facility used to simulate expected conditions in a chemical plant; (a) bench scale unit (b) 40-gal unit.
Corrosion under Heat Transfer Conditions

It was mentioned in the previous section that, in testing for velocity effects, a source of heat is introduced into the process test fluid. The method of introducing the heat and its effect on the surface through which heat was transferred gave rise to the early work of corrosion under heat transfer conditions. One looks to the early work of the Atomic Energy personnel at the Hanford works of General Electric, citing such names as Scharfstein, Groves, Eisenbrown, and others, in addition to Fontana's publications in "I and EC" on this subject and the work by Fisher and Whitney in NACE publications.

In the process industry, work with heat exchangers established at an early date that the surface through which heat was being transferred to bring the temperature of the solution to a given value corroded at a more rapid rate than the surface of the same metal merely exposed in the process fluid. Since heat exchangers and similar heat transfer devices represented not only large investment on the part of manufacturers of chemicals, but also critical items where the failure of such an item would shut down the process, it became necessary to know this influence.

The old rule of physical chemistry about doubling the reaction rate for every 10 deg C increase in temperature still holds true; this applies to the difference in corrosion between a sample at one temperature and a sample at another temperature. This is not, however, an accurate rule for predicting the corrosion rate under heat transfer conditions. The reason for this lies with the nature of heat transfer to a process fluid; in this transfer process the surface temperature of the metal through which heat is being transferred is higher than the solution temperature due to the presence of surface films on the process fluid side which serve to act as barriers or resistances to that flow. The rate of heat input to the metal surface, and the rate of heat removal from the metal surface, are important variables, governing to a large extent the temperature of the surface where the heat is being transferred.

Currently, National Association of Corrosion Engineers, through Committee T-5A have established a test procedure⁴ which allows these variables to be evaluated. The test procedures used by the early experimenters at AEC and Ohio State University, in particular, are the basis for this corrosion testing standard. The usual technique is to use a high wattage soldering iron whose heating surface is a flat disk coupled to an aluminum block, used for good heat transfer and for the measurement of the rate of heat transfer, and ultimately coupled to a corrosion specimen which serves as the cover to an opening in the test vessel. The use of thin-gage thermocouples serves to measure both the rate of heat transfer and to approximate the tempera-

⁴ Laboratory Corrosion Testing of Metals Under Heat Transfer Conditions, (Number not yet assigned by NACE Technical Practices Committee T-5A-6b).

ture of the metal surface to which the heat is being transferred. In most test methods, a duplicate specimen is used at the interface between the liquid and vapor phases to transfer heat, with a third duplicate specimen attached to a cold finger to remove heat. Proper gasketing is necessary and agitation of the process fluid is also required. Corrosion rate can be determined by weight loss for the area of the specimen exposed to the heating fluid. In addition, pit depth can be quantitatively measured, as can any other variables relative to corrosion, such as intergranular corrosion, sensitivation effects, crevice corrosion, etc.

Welding Effects on Corrosion in Process Fluids

It had been mentioned earlier that welded specimens can be used as part of the INCO Test Spool, and indeed this has been done in many cases. However, because the specimen is made up partially of unwelded and partially of welded material, it has been difficult to establish an absolute quantitative corrosion rate for the welded portion only. Furthermore, it should be recognized that there are variations metallurgically across a weld. This becomes evident when one considers that the weld bead represents molten metal at the time of welding, and the temperatures in welding therefore go all the way from the melting point of the material being welded (or the weld rod) to the base metal away from the bead which stays at ambient temperature. The distance over which the welding operation has a metallurgical influence is a function of the material being welded and the welding rod, the heat input and such factors as thermal conductivity, mass of material, etc.

Work with 18-8 austenitic stainless steels relative to their then unpredictable corrosion behavior when welded, brought about the early Strauss test [7] (copper sulfate as a corrodent) and the Huey test [8] (boiling nitric acid) to determine the susceptibility to intergranular corrosion. Currently, ASTM A 262–70, Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels, covers not only the boiling nitric acid test, but also the electrolytic oxalic test. The extensive use of stainless steel in the largest chemical company in the country, namely, E. I. duPont de Nemours, led to much work on the part of researchers at duPont on tests that would be shorter and more definitive than the Huey and Strauss tests. This has culminated particularly in the work by Michael Streicher and the oxalic etching test [9]. This test allows a purchaser to determine the relative corrosion resistance of welds of the material in various media before fabricating the material and putting it in service.

The less refined method to determine the behavior of stainless steel in its welded conditions in a quantitative fashion, is to sensitize the sample before exposing it to the corrosive environment on an INCO Test Spool. For an austenitic stainless steel, this consists of heating the sample in the 800 to 1200 F range where carbides precipitate and where, therefore, the

matrix is deprived of the chromium and nickel necessary for corrosion resistance. The entire specimen behaves as if it were the critical part of weld, namely, the sensitized zone of carbide precipitation in the weld.

In titanium and zirconium in certain environments, a galvanic effect between the large grains of the weld bead and the small grain size of the base metal has been observed. The large grain size is preferentially corroded in these environments. Since this is a galvanic effect, it would have to be tested in a fashion described above for galvanic corrosion.

Electrochemical Techniques

While the resistance probe technique is truly not an electrochemical method for determining corrosion, it serves essentially as an intermediate step between weight loss specimens and true electrochemical techniques and, as such, will be briefly described. The resistance probe works on the basis that the electrical resistance of a thin metal specimen varies directly with the thickness of that section: consequently, as the thin cross-sectional area is corroded, the resistance of the probe changes. This resistance can be read indirectly without weighing the specimen via the standard Wheatstone Bridge circuit and correlated with loss in thickness per unit time. This means, therefore, that resistance probes can be read while they are completely immersed in a process stream without the necessity for removal from the stream. Furthermore, the change in resistance can be fed to a recording device and the behavior of the process stream, relative to one or more resistance probes, can be recorded for a continuing view of process variables. Such resistance probes, therefore, work to determine variations in process streams, such as absence of inhibitor, presence of oxygen, upset conditions. There has been great difficulty on the part of researchers in the process industries, however, to correlate the corrosion rate as indicated by the resistance probe in its fully immersed conditions in the process stream with the rate determined by the behavior of the walls of a vessel or a pipe. There is generally good correlation between a resistance probe and a sample on an INCO Test Spool since both are immersed in the bulk solution and do not represent conditions of heat transfer through the specimens. For extremely sensitive conditions, such as the presence of water in what is required to be an anhydrous solution (for example, dry hydrogen chloride), a resistance probe of the right metal serves as an excellent warning device of leakage of moisture through a pump seal or a failure of a heat exchanger tube, etc. Probes can be made by individuals, or they are procurable from at least two major sources in the United States.

The true electrochemical techniques are those involving the potentiostat and the galvanostat, both of which essentially represent determinations of current versus potential or potential versus current of a given metal in a given environment. For several years both of these techniques were laboratory oriented and were quite useful in determining fundamentals of corrosion behavior. In fact, the work of Stern and Wissenberg which led to the development of the 0.2-percent palladium alloy of titanium was done along these lines [10]. Much has been written in the literature on the exacting techniques involved; in view of the fact that there are numerous models in the market, many of which differ primarily in their electronics, a detailed discussion will not be presented.

Fontana and Greene have a chapter dealing with "Modern Theory-Applications" which discusses electrochemical methods used to determine corrosion rate [5]. This should serve as an excellent reference for those who are interested in this approach. They summarize the advantages of electrochemical corrosion rate measurements, particularly linear-polarization techniques, as

- 1. They permit rapid corrosion rate measurements and can be used to monitor corrosion rate in various process streams.
- 2. These techniques can be used to accurately measure very low corrosion rate (less than 0.1 mpy) which are both difficult and tedious to perform with conventional weight loss or chemical analytical techniques. The measurement of low corrosion rates is particularly important in nuclear, pharmaceutical, and food processing industries, where trace impurities are problems.
- 3. Electrochemical corrosion rate measurements may be used to measure the corrosion rate of structures which cannot be visually inspected or subjected to weight loss tests. Underground tanks and pipes and large chemical plant components are examples.

The American Society for Testing and Materials has established two recommended practices that pertain to electrochemical techniques. G 3-68 is the Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing; this deals with reporting and displaying electrochemical measurements. G 5-71 is the Recommended Practice for a Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements; this covers experimental procedures that lead to repetitive results when conducted by different researchers in different laboratories.

The widest use industrially of electrochemical principals of corrosion has been that of anodic protection. This is a procedure first commercially developed by researchers at Continental Oil Company and since reported by many others; however, it was a paper by C. Edeleanu of England in 1954 that first called attention to anodic protection [11]. Its techniques are not applicable to all solutions; it has found widest use involving steel in concentrated sulfuric acid. While anodic protection is beginning to play an important role in certain segments of the chemical process industry, its somewhat limited involvement has not yet resulted in any standards being developed for its use. Contrariwise, the more widely used technique of cathodic protection, both applied to underground structures such as pipelines and tanks and also to process fluids and their containers, has been evident in many standards, particularly by the National Association of Corrosion Engineers and from the work of NACE by the Department of Transportation and other regulatory bodies who are concerned with corrosion on underground units transporting dangerous fluids.

NACE Standard, RP-01-69, is the recommended practice for Control of External Corrosion on Underground or Submerged Metallic Systems. Much of this has now appeared in an American National Standards Institute Specification (ANSI) B31.4-1971 for liquid petroleum transportation. An earlier standard on gas transmission and distribution piping systems, USASI B31.8-1968, also has sections dealing with standard methods of determining cathodic protection requirements and the measurement of this protection.

Elevated Temperature Corrosion

The INCO Test Spool cannot be used for temperatures above 500 F because of the breakdown of the plastic insulators between specimens. This is the maximum temperature if Teflon is used; if phenolic spacers are used, a lower temperature limit of 300 F must be established. However, it is possible to adapt the INCO Test Spool by using either ceramic insulators or by ignoring the concept of insulators entirely and by recognizing that at temperatures of over 800 F oxidation effects will be more critical than any electrolytic dissimilar metal effects. Thus, where aqueous or conductive solutions are not a factor, INCO Test Spools have been prepared for use at elevated temperatures and have given excellent results. The techniques of evaluation are a variation on those in the conventional spool in the sense that with oxidation effects there is usually a weight gain rather than weight loss. Thus, it is oftentimes required to do a metallurgical cross-section study of the depth of oxidation, the amount of metal remaining unaffected, and therefore the load-carrying capacity at the end of the test. In practice, ultrasonic and eddy current techniques can be used with certain alloys to determine the amount of the material affected by the high temperature. These nondestructive techniques, it should be pointed out, can also be used in other phases of corrosion control. Particularly, eddy current techniques, as exemplified by the Probolog or the Introview,⁵ are excellent in determining localized corrosion of alloying elements as in dezincification, and general corrosion loss from equipment such as pipe and tubing. Not to be forgotten also are calipers that have been developed for inside wall tubing measurement, though in a sense, this represents physical dimensioning and thus falls into the category of corrosion rate determined by any dimensional change in a given period of time.

Section 3.4.6 of Recommended Practice G 4 (Conducting Plant Corrosion Tests) deals with the use of a bayonnet heater to determine the hot wall effect in plant corrosion tests. Recommended Practice for Aqueous Corro-

⁵ Probolog is an instrument manufactured and sold by Branson Instruments Co., Stamford, Conn. Introview is an instrument manufactured and sold by Sperry Gyroscope Co. Ltd., London, England.

sion Testing of Samples of Zirconium and Zirconium Alloys, ASTM G 2–67, contains procedures for the evaluation of these materials at elevated temperatures and pressures including a pickling procedure for preparation of the specimens. NACE Standard TM-01-71 deals with Autoclave Corrosion Testing of Metals in High Temperature Water.

Localized Corrosion

Localized corrosion exists in many forms such as pitting, crevice corrosion, filiform (underfilm), exfoliation, fatigue, and intergranular corrosion. In most cases, the detection of one or more of these forms of corrosion is best done visually, though in certain cases magnification from an optical microscope is necessary. Crevice corrosion is often called contact or concentration cell, deposit, differential, aeration, gasket, interface, poultice, water line, or wedge corrosion. It is a form of localized attack that occurs at shielded areas on metal surfaces exposed to particular solutions. Usually this corrosion occurs because of the design. Examples include spot-welded lap joints, threaded or riveted connections, gasket fittings, porous welds, valve seats, coiled or stacked sheet metal, marine or debris deposits, or meniscus at a water line. The cure of such corrosion is often based in changes in design.

Two recent symposia have taken place on this subject. One was the Symposium on Localized Corrosion at the ASTM annual meeting at Atlantic City, June 1971, and the other the U. R. Evans International Conference on Localized Corrosion held at Williamsburg, Virginia, in December 1971. A paper by W. D. France, Jr. [12] on Crevice Corrosion of Metals was presented at the first conference, dealing specifically with crevice corrosion of metals but touching also on other types of localized corrosion. This serves as an excellent bibliography on most metal systems that have been discussed in this field.

F. L. LaQue presented the keynote speech at the Evans Conference on "The Problem of Localized Corrosion: What is it, its Extent, its Causes, its Cures and What Needs to be Done." It suffices to say at this time that there are no accepted standards of testing for localized corrosion. Examples have been given earlier in this paper; both references cited above have further examples.

Low Temperature Measurement

Since the corrosion rate generally, as was stated earlier, is doubled for every 10-deg C rise in temperature, one would therefore not have to worry about corrosion at low temperatures, other than for the effects of condensation on the surface, plus any possible metallurgical changes. However, the corrosion engineer working with cryogenic materials must be cognizant of the impact strength loss at low (below room) temperatures with certain alloys. While this is not basically a corrosion phenomenon, it is a concern of the materials engineer in the chemical industry. Condensation effects or the corrosion on a cold surface can be determined, as was discussed earlier, in a laboratory hot wall tester by the use of a cold finger on a metal test surface allowing condensation of the corrodents to occur on that surface and determining the corrosion in the conventional fashion. Embrittlement may be determined by use of an Izod or Charpy pendulum impact tester. The metallurgical changes in a weld must also be evaluated for impact behavior at low temperatures. Certain plastics also become impact-sensitive at lower than ambient temperatures so that their use at lower than normal temperatures becomes delicate. In addition, the greater coefficient of contraction (and expansion, on heating) of many unreinforced thermoplastics requires proper design (expansion joints or loops for long straight runs) to avoid mechanical failures.

Process Evaluation of Other Materials

Materials other than metals do not corrode in the accepted electrochemical sense, since they do not have metallic ions which can go into solution; rather they deteriorate and are no longer usable under certain conditions. The types of deterioration can be similar to corrosion; for example, certain plastic materials stress crack in the presence of certain organic solutions. There can be the equivalent of metasomatic corrosion with certain parts of the composite nonmetallic materials being leached out. The testing of nonmetallic materials for their corrosion resistance can largely follow that used for metals in terms of Recommended Practice G 4 on Conducting Plant Corrosion Tests, except that the evaluation of the nonmetallic materials is along a different path than that of metallic materials. Since many nonmetallic materials do not lose weight in certain corrodents, but gain weight, obviously then, the use of mdd or ipy as a way of reporting results has no great meaning. The preferred technique of evaluating nonmetallic materials, irrespective of how they are exposed, is the change of physical properties. Such properties can include tensile strength, yield strength, flexural strength, hardness, elasticity, etc. The American Society of Testing and Materials has many standards that pertain to the measurement of these properties for a given material and obviously such standards and procedures should be followed.

Perhaps one of the more widely used properties because of its simplicity and rapidity is the flexural strength evaluation. This test is quite similar to that for cast iron in A 48–48 in that the sample is flexed at the center by the application of a load; the sample is supported as a simple beam at two points equidistant from the application of the load. However, in the case of plastics and other nonmetallics, conditioning after removal from the environment and before testing, is critical in terms of establishing equilibrium with the given temperature and humidity conditions.

This matter of testing reinforced plastics has now manifested itself as a

National Bureau of Standards Voluntary Product Standard, P-15-69, called Custom Contact Molded Reinforced Polyester Chemical Resistance Process Equipment. Section 10 of that standard deals with chemical resistance and describes part of ASTM C 581-68, Test for Chemical Resistance of Thermosetting Resins Used in Glass Fiber Reinforced Structures. This method is based on a test procedure developed by the Reinforced Plastic Corrosion Resistant Structures subcommittee of the Society of the Plastics Industry, and stems from the early work at duPont of Harvey Atkinson and Robert Webster. ASTM Committee C-3 on Nonmetallic Materials has been active in this area.

C 581-68 requires that the test laminate be cured at room temperature for 16 h to a Barcol hardness equal to the resin manufacturer's minimum specified hardness for the cured resin. Tests are to be conducted under one or more specified temperatures as well as the reflux temperature and the required service temperature. Twenty-three corrodents are suggested for use in obtaining general comparative chemical resistance data under nonagitated, static conditions. The properties to be evaluated are determined on specimens immersed in the test solutions for 30, 90, 180 days and 1 year for one set of control specimens immediately following the cure period. In addition, another set of specimens which have been aged in air at the test temperature for the total test period are used as controls. The properties to be determined are the change in thickness, change in Barcol hardness, change in flexural strength and flexural modulus, and change in appearance. These are determined at each time interval, with appearance observance including any surface changes, color changes, obvious softening or hardening, crazing, lamination, exposure of fibers, or other effects indicative of complete degradation or potential failure.

The flexural test in the specification of the Bureau of Standards can also be used on other nonmetallics such as impregnated graphite, impregnated wood, rubber, other plastics, and under some controlled conditions, concrete.

Tests for Lining Materials

A lining material is usually an organic or metallic thin film applied by one of several means on a substrate. Since the substrate will not be exposed to the environment in service, with the unlined (outside) side of the lined substrate usually exposed to ambient condition, then it is not proper to test lined steel or other metallic panels by full immersion or dunking. Such dunk testing does not take into account the heat transfer through the specimen to the surroundings and also the flexural variations that occur because of temperature differentials both inside and outside the solution. It was for this reason that the National Association of Corrosion Engineers through Unit Committee T-6 has established a proposed standard test method entitled Laboratory Method for Evaluating Protective Coating for Use as Lining Material in Immersion Service (no number assigned yet). This method consists of exposing one size of a coated panel to environmental conditions closely approximating those which are encountered under actual service conditions. This test method, unlike other tests, closely simulates the phenomenon found in service involving temperature differentials between the external and the internal surfaces of the coating: these differences may accelerate the permeation of the coating by the corrosive medium. This work was originally presented in a technical journal in the article, "An Improved Method for Evaluating of Tank-lining Systems" by A. F. Torres and S. S. Feuer, then of Atlas Chemical Industries [13].

Basically, the test cell normally consists of a 6 in. in diameter open cylinder of Pyrex with a 4-in. minimum length and several side connections; steel plates coated on one side with the lining to be tested are used to close the open ends of the cylinder. The solution that serves as the environment is introduced and heated internally, with a condenser attached to one of the cylinder side connections to prevent evaporation of solution. Exposure of the lining is for one face (the lining), exactly as in an actual tank. By proper volume of solution, size of cylinder and size of plate, the ratio of the surface area of the lining to the volume of the solution in the test cell can be made to approximate that found in service conditions in a tank, drum, tank truck, tank car, barge, etc.

Not only is this test used for lining materials but it is appropriate to evaluate any material used as a vessel. This includes resin and fiberglass and metals. It should be recognized, in the case of testing metals in this fashion, that weight loss considerations would not be valid; instead, it is necessary to check for pitting, crevice corrosion, loss in thickness, and more particularly, pickup of metallic ions from the metal surface in the corrodent. Oftentimes, in the chemical industry for determining the proper material for a storage vessel, it is necessary to check the change in color of the solution under standard exposure conditions. In this regard, it should be recognized that slight corrosion which is not measureable in conventional techniques, can cause a catalytic reaction of certain organic materials resulting in their deviation from water-white appearance. The use of color testing comparators, such as the American Public Health Association Colorimeter, is often used in this regard.

Atmospheric Effects

In LaQue's paper on corrosion testing referred to earlier, there is a fine historical discussion of the early work of ASTM over the controversy regarding the relative merits of different kinds of iron and steel in resisting atmospheric corrosion. Around the turn of the century, Committee U (later to become Committee A-5) reported on some of their early tests of the different kinds of iron and steels exposed to an accelerated acid test, as well as exposed to industrial and marine atmospheres. This early work led to a round-robin test work on the part of steel and other metal producers, as well as metal users. The late C. P. Larrabee, of the then Carnegie-Illinois Steel Corporation, has a chapter in Uhlig's *Corrosion Handbook* dealing with this matter [14]. Larrabee indicates that most corrosion investigators in the USA followed the procedures of ASTM Committee A-5 and exposed specimens at an angle of 30 deg to the horizontal facing south. Four by six inch specimens were nominally used, mounted on porcelain insulators to prevent galvanic effects. Conventionally, 70 specimens are accommodated in an area roughly 68 in. long and 38 in. wide. Larrabee indicated that nonferrous metals are exposed vertically by ASTM Committee B-3 while many tests of painted specimens are exposed at a 45-deg angle.

R. K. Swandby, formerly of International Nickel and Wyandotte Chemical Corporation, in a chapter in LaQue and Copson's book indicates that "the degree that a metal or alloy is exposed to the atmosphere also plays an important part in the severity of attack [15]. Many materials exposed directly to the atmosphere are not attacked as severely as the materials partially sheltered. The probable reason for this is that the partially sheltered materials remain wet from dew for longer periods of time. They also do not receive the beneficial effects of washing by rain."

Of particular significance which should be mentioned in regard to atmospheric corrosion testing and the results thereof is the famous atmospheric test site of International Nickel at Kure Beach, North Carolina. One of two locations is 80 ft from the Atlantic Ocean water line and the other is 800 ft. Duplicate specimens are exposed in both lots to get comparative effects of the severity of salt spray and moisture on the various materials. A direct offshoot of this testing of atmospheric materials is the development of the low-alloy, high-strength steels to ASTM Standard A 242, popularly known by trade names such as Cor-ten and Mayari-R⁶ among others. These materials are widely used in many atmospheric exposures, including chemical plants, in their unpainted, natural conditions. Not only are there savings in paint costs but also the weight (cross-section) can be reduced to take advantage of the higher strength. Over the years, countless atmospheric tests have been made at many locations around the world, so that comparative results now are available both with regard to the materials and to the environments.

Other committees of ASTM, as well as NACE and the Federation of Paint Societies, have evaluated the atmospheric resistance of paints and protective coatings; for chemical plant environments, the most widely accepted test specimen is the KTA panel. This was devised by the late Kenneth Tator, the leading industrial paint testing consultant in the USA, and exists in several variations. Essentially, a KTA panel consists of a piece

⁶ Cor-ten is a trade mark of the United States Steel Corporation. Mayari-R is a trade mark of the Bethlehem Steel Corporation.

of $\frac{1}{8}$ -in. steel, approximately 4 by 6 in., to which is welded a piece of channel iron. The weld purposely is a skip-weld and is rough; all sharp edges are kept as such and not rounded. Surface preparation is varied to meet industrial test requirements. After the panel is coated, it is scribed down to the surface as well as being impacted. Thus, one ends up with steel that has most of the common industrial deficiencies, so far as design for protective coatings is concerned-skip welds, sharp edges, pockets, impact area, scribe, corners, pits, planes, etc. Rating of such panels is done on a comparative basis of 0 to 10 for each potential location of failure as a function of time of exposure. Size of panels and construction can vary depending on space requirements and the number of systems to be tested. The ultimate in such testing was Texas-style; individual 55-gallon drums blasted and coated with individual paint systems and arranged in a ¹/₂-acre field. Inspection of the finished paint system before exposure is requisite to avoid a lack of correlation between laboratory preparation of panels and industrial application of paint on structures.

Corrosion Control

Many years ago, one of the early undergraduate texts which dealt with materials indicated that there were three ways of stopping corrosion. These were:

- 1. Change the materials
- 2. Change the environment
- 3. Protect the material

As advances have been made in corrosion science and engineering, one should also add several other factors in controlling or stopping corrosion that include the following:

- 1. Improve the design
- 2. Develop improved testing methods
- 3. Tighten existing specifications
- 4. Improve inspection of equipment
- 5. Share common corrosion experiences
- 6. Join appropriate technical societies to disseminate the above knowledge.

Certain of these items are self-evident; others need more detailed explanation. For example, with regard to changing the materials as a way of stopping corrosion, this is usually the step that a novice would undertake in his lack of corrosion fundamentals. There are still those who consider that upgrading to a stainless steel is a solution to all corrosion problems! Obviously, this is not the case; otherwise, there would not be so many materials of construction on the market. However, by upgrading to the proper material of construction, one can often avoid, or at least minimize, the effect of a given environment. Since it is not the purpose of this chapter

to go into all the ramifications of alternate materials of construction, the matter cannot be properly pursued. It suffices to say that the gamut of materials of construction, as indicated earlier, range all the way from steel and cast iron through stainlesses, high nickel alloys, copper-base, aluminum-base, nickel-base, titanium, zirconium, precious metals, and ultimately into the entire field of nonmetallics which can include glass. Not that glass is the ultimate material of construction, but it does have a very wide range of chemical resistance to all but strongly alkaline and acid conditions involving HF and HCl. As indicated earlier, the fragility problem with glass had been a problem until Corning Glass Company, in particular, developed their armourized material which uses an epoxy-fiberglass coating on the exterior. In addition, they were very ingenious in developing a ball joint that allowed flanges to be slightly misaligned and still not put undue stress and incipient failure on the part.

The matter of changing the environment is one that leads automatically into the field in inhibitors. It is not always possible to change major process conditions, but there is often the feasibility of adding a small amount of an independent material which would minimize corrosion. Environmental changes which can take place to reduce corrosion include change in temperature and pressure, agitation, aeration, etc. One of the many variables which can be controlled to change the environment is that of the addition of one or more compounds which change the surface characteristics of the metal exposed to the environment. Such compounds are usually called inhibitors in the sense that they reduce the corrosion rate of a metal in a given environment. These inhibitors can be organic or inorganic in nature and, as indicated, are usually specific for a given metal in a given compound. There are several fine sources of the behavior of specific compounds and the metals which they inhibit to be found in the literature; these include the data in Uhlig's Corrosion Handbook [14] as well as in Fontana and Greene [5] and in the Russian book called *Metallic Corrosion Inhibitors* by Putilova, Balezin, and Barannik [16]. Inhibitors have been widely used in the past in cooling water circuits because of the closed nature and therefore fixed amount of water to be inhibited. Under conditions of a closed loop, as opposed to an open or continuous flow-through circuit, the economics of inhibitors are well established. One generally speaks in terms of a tenth of a percent by weight or less of inhibitor relative to the concentration of the major corrodent. Even at this low concentration in a once-through circuit, inhibitors are generally too expensive to be used. Until the recent upsurge of interst in the toxic effects of chromates on plant and water life, sodium chromate was a very widely used inhibitor to prevent attack of aerated water on iron and steel. Other materials have been substituted for chromate such as nitrites, nitrates, phosphates and silicates, sometimes singly and sometimes in combination. It should be noted that what is an inhibitor for one material is oftentimes an accelerator for another material. Thus,

amines are relatively effective on steel but because of their ammonia complex, under certain conditions of temperature, concentration, and design, they can cause stress corrosion cracking of copper-base materials.

The organic, the physical, and the electrochemists have had great opportunities, and have taken advantage of these opportunities, to investigate corrosion mechanisms and develop corrosion inhibitors, particularly using the technique of the potentiostat for this work. Noteworthy among these investigators have been Norman Hackerman, formerly of the University of Texas, and his students and colleagues in this field. Certain organic compounds have been discovered and investigated which make effective inhibitors; these include thiourea and certain benzoates. There are many companies who specialize in the development and manufacture of inhibitors for particular metals in specific environments. These materials lend themselves widely to certain production operations.

There was a class of inhibitors first discovered and developed by Wachter and colleagues at Shell Development Corporation that worked in the vapor phase, rather than in the liquid phase, in preventing the formation of oxidation and rust on common metals [17]. These vapor phase inhibitors are generally organic in nature and have in common a relatively high volatility from the crystalline solid material. The component is generally an amine in nature and can be applied by any one of several techniques. Crystals of the VPI (Vapor Phase Inhibitor, used by Shell Development as a trade name) can be placed in an open container in a closed vessel; it will be found that the interior surfaces of this vessel will not develop rust or oxide even if water vapor or oxygen enter the vessel. As such, vapor phase inhibitors have been used to maintain standby equipment such as boilers, turbines, etc. in prime condition without the necessity of having to do any cleaning when these units are put back on the line. The vapor phase inhibitor can also be applied by fogging a solution containing the crystals into the container where the solid inhibitor crystallizes and puts a mono-molecular film on the surface of the container. Other techniques have involved the impregnation of paper with the inhibitor so that a delicate part, such as a ball bearing, can be wrapped in the inhibited impregnated paper and sealed in paper or a plastic film that does not allow the vapor phase inhibitor to rapidly dissipate to the atmosphere. Such parts can then be stored for quite some time in humid conditions without rusting occurring. Quite obviously, the military is interested in such inhibitors for the storage and maintenance of critical equipment under humid conditions, such as is found in many parts of the world.

Where it is impractical, for any one of several reasons which may include economics as well as ease of fabrication, to change the material or to add an inhibitor, then the materials engineer may choose to use a protective coating on an inexpensive substrate. The purpose of the coating is to act as a nonreactive barrier between the environment and substrate. For this reason, the coating preferably should be impervious to the environment, it should be continuous (free of voids or pin holes), and it should be sufficiently durable to withstand the temperature and process conditions of the environment. A differentiation is made in corrosion circles between a coating which is used for atmospheric exposure, and a lining which is used for immersion conditions. While it is true that coatings and linings have much in common and may often be applied by the same skilled trades, nonetheless, there is sufficient difference in terms of the severity of corrosive conditions between a coating and a lining that special requirements exist for both, including application procedures. There are many committees of the National Association of Corrosion Engineers that have been involved in these problems: basically, Technical Practices Committee T-6 with its various subcommittees has dealt with coatings for atmospheric conditions and linings for immersion conditions including all the ramifications of surface preparation. It should be recognized that linings can differ from coatings in the sense that linings include not only material applied as a liquid which converts to a solid in one of several fashions, but also solid materials themselves. For example, one would speak of a sheet lining of rubber or plastic, and one could also speak of a lining that was made up of a solid membrane plus chemically resistant brick and mortar construction. Irrespective of whether the lining is applied as a solution and then converted to a solid (this is done by any one combination of three techniques that include drying by oxidation, drying by solvent evaporation, and drying by catalysis), it is requisite that the resulting lining material be resistant chemically to the environment to which it is in contact. Since most conventional linings are organic in nature, one has to be careful of their use with organic solvents. The adage to be applied in this case is "when in doubt, test." Of course, testing should be carried out, as indicated earlier, so as to avoid any obvious erroneous conclusions due to faulty testing techniques. One lining worthy of mention because of its wide applicability is that based on glass flakes dispersed usually in a polyester resin; this can be applied as a spray with a high pressure pump gun or can be troweled on the surface. In a case of the spray the catalyst is applied simultaneously with the polyester resin glass flake mixture, while in the case of troweling the catalyst is mixed in with the viscous mixture of flake and resin in a batch fashion. Depending upon the size of flakes and the finishing operation the flakes may or may not be rolled as they are applied to the surface (currently, the larger size glass flakes are rolled after application to take on an overlapping parallel position to the substrate like fish scales; smaller flakes are not rolled and exist in their random position). The resistance of this material is quite outstanding particularly to many inorganic environments. There are other combinations of reinforcing materials and resin binders such as glass mat and glass cloth with epoxy resins, polyester resins and even furan resins; much of the technology with these materials is similar to that of the monolithic reinforced plastic construction, except that when these materials are used as a lining, the difference in expansion coefficient of the reinforced plastic lining and the substrate must be taken into account if there are sizable temperature extremes. A material that offers superb corrosion resistance is not particularly good if it cracks because its expansion was greater than that of the vessel in which it was installed—a failure is a failure, irrespective of whether it was due to corrosion or due to mechanical problems such as thermal expansion or contraction.

With regard to control of corrosion by coatings, it should be indicated that the present experience in the chemical industry, as well as in variations of the chemical industry, such as, petrochemical, pulp and paper, fertilizer, etc., has established that a zinc-rich primer with protective top coats offers the longest maintenance-free life provided there is continuous inspection and patch repair. These zinc-rich primers are either organic or inorganic in nature. The inorganic primers are generally based on silicates of one form or another, with a very finely divided zinc powder at approximately a 90 percent by weight basis. This material must be applied on blasted steel (free of mill scale and rust). Depending upon the silicate the curing often takes place under moist conditions. The organic zinc-rich primers are generally based on chlorinated rubber or catalyzed epoxy resins; a blasted surface, free of moisture, must be used. It is important that all the solvent be removed from the primer and that the primer be completely dry before being topcoated; otherwise, blisters and mudcracking may form. The topcoats for inorganic zinc primer and organic zinc primer are usually chosen from those based on vinyl resins, catalyzed epoxy resins, or chlorinated rubber resins, often depending upon the environment to which the coated steel will be subjected and to the temperature. There are many advantages to each of these topcoats and the materials engineer will do well to balance ease of application, foolproof application, ease of topcoating with a second coat, ease of repair, maintenance of gloss and cost, taking all these factors into account. The use of the zinc-rich primers is based on the cathodic protection given to localized breaks in the primer and the bare steel. While this is true in theory, nonetheless one must balance the aggressiveness or the conductivity of the environment against the particular zinc primer used and the frequency of repair. Let it be categorically stated that in an aggressive environment, even the best protective coating system requires continuous inspection and patch repair; the better the system, the less frequent and smaller the amount of repairs to be made. A protective coating system in a strong chemical environment should not be expected to have an indefinite life. A long life, yes, but an indefinite life, no.

Changing the material obviously can be used to control corrosion in the sense that for most environments, even the most aggressive, there can be found a material perhaps at a great cost which is resistant to that environment. Thus, in the melting of glass to form fiberglass, where temperatures in excess of 3000 F are involved with oxidization, the material of construction of the container for the molten glass is platinum. Here one needs resistance to oxidation and maintenance of hole size with resistance to abrasion of the flowing glass. While this may be an extreme, the fiberglass industry would not use platinum if less expensive materials would do the job. Long continuous maintenance-free life is required and platinum has been found to be the one material that will do this job. Advances have been made with other of the high melting point materials such as tantalum, columbium, hafnium, and tungsten, such that in many specific corrosive environments these materials may be used often as a deposit on a less expensive and less resistant substrate. Techniques have been developed for the deposition of these materials usually from fused salts so as to achieve the chemical resistance of the expensive high density materials without the cost of these materials in their solid form. Periodically, interest revives in deposits on nickel on steel, usually when there is a critical nickel shortage. Historically, one looks back to the story of the uranium hexafluoride diffusion plant at Oak Ridge for the widespread use of the electrodeposited nickel on the inside of steel tubes to provide the corrosion resistance of nickel at a lesser cost and greater availability than solid nickel. At one time, there was a major producer in the United States who made sheet steel coated with 10 or 20 mils of electrodeposited nickel of one or both sides; this steel could then be rolled and fabricated (including welding) in the technique quite similar to that of sheet steel. Other developments that have taken place over the years included the development of the electrode-less nickel conventionally known by the General American Transportation Corporation trade name, Kanigen. This material held great promise for the caustic soda industry until problems began to develop in the adhesion of the electrode-less deposited nickel on other than sandblasted surfaces. In addition, repair techniques were somewhat difficult for large vessels. The best source for authoritative and quick information on alternate materials of construction for a given chemical environment is that found in the book published by the National Association of Corrosion Engineers, entitled Corrosion Data Survey. Here, for a given environment (environments are thoroughly referenced by the chemical radical involved), one finds the famous Nelson chart, correlating temperature and concentration of environment and the corresponding symbol for corrosion rate of approximately 20+ metals. Volume V of Corrosion Data Survey will be in two parts, one concerned with metals and the other concerned with nonmetals. As indicated earlier, the gamut of metals surveyed in this book is quite thorough, since it represents the work of contributors across the industries of the United States and Canada.

Electrochemical Methods

In the section on Standards and Testing, both cathodic and anodic protection were discussed as being applied in many industrial situations; they represent a variation of protection of the substrate by other than a lining or a coating. While cathodic protection has been most widely applied to buried tanks, hydraulic elevator shafts, and pipes and related underground structures, applying the principles of cathodic protection can allow its use to tank interiors and even in certain circumstances the interior of pipes. At the 4th International Corrosion Conference on Metallic Corrosion in Amsterdam, there was a report on the application of anodic protection to the interior of titanium heat exchanger tubes handling a reducing viscose solution that was most corrosive to titanium in the absence of the impressed electrical current [18]. In addition, the solution was so corrosive that no other metal was practical for this service; difficulties had been found in impregnated graphite tubing because of fouling and fragility. Changing the potential of a surface from a region in which the surface is active to a region in which it is passive can be used under many conditions to effectively control corrosion.

Major Trends and Problems

The corrosion engineer in the chemical industry is continuously faced with a problem that has ever bothered all engineers, irrespective of the industry in which they are located; namely, how to update engineering knowledge with the scientific developments that have been brought forth by others. One has only to look at the pages of the NACE publication, *Corrosion*, or the section in the ASM-AIME publication, *Metallurgical Transactions* dealing with transport phenomena, to realize that monthly, if not daily, great steps are being made in the field of materials science. More than ever before, it is necessary to coordinate the activities of the materials engineer with those of the materials scientist. Several years ago, such an attempt was made by personnel at the National Bureau of Standards and personnel from the Office of Naval Research when a conference bridging the gap between theoretical and applied corrosion was held in Washington with great success [19].

Most noteworthy, however, have been the developments in electrochemistry as applied to theoretical and ultimately to practical corrosion problems. It behooves the corrosion and materials engineer to remain alert to the theoretical developments and incorporate them in his practical thinking and doing. The very fact that in many universities and engineering schools there has been a decided trend towards a Department of Materials Science and Engineering is indicative of the trend taking place toward making the materials engineer a well-rounded man. In many universities, the materials scientist and materials engineer are grounded in the basic and current theory of metallurgy, polymers, and ceramics. It may be assumed then, that the future corrosion engineer will be at home in organic polymer chemistry, in metallurgy of all alloys for the complete gamut of temperature and physical requirements, and in nonmetallics, such as glass, ceramics and graphite, along with knowledge of electrochemistry as it relates to the corrosion phenomenon and as it relates to cathodic and anodic polarization.

Today, the fact that engineering students in the United States can now take more than one course at a university in the field of corrosion is quite an achievement. So far as is known at the present time, a student would not receive a degree in corrosion engineering but perhaps would receive his degree in metallurgical engineering with a specialty in corrosion, or more particularly, a degree in materials engineering with a specialty in corrosion. In fields such as engineering the demand on a student's time for fundamental and theoretical courses in all engineering disciplines, and fields such as humanities, mathematics, and physics, are such that it is often difficult for such a student to get a thorough grounding in materials or corrosion engineering by actual undergraduate course work. The work that the National Association of Corrosion Engineers has done in publishing a lecture and home study course on basic corrosion engineering [20], as well as the course which Dr. Fontana has written and given for the American Society of Metals on Corrosion [21], is a technique by which the graduate engineer and others may grasp the fundamentals of corrosion and materials engineering. That, along with special graduate courses, is a procedure the practicing engineer can use to improve his knowledge of the field.

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Chapter 10

Corrosion Standards and Control in the Nonferrous Metals Industry

W. H. $Ailor^1$

Industrial Corrosion Test Standards

Nonferrous metals are used in a wide variety of applications: architectural and structural uses, as coatings for other metals or materials, as electrical conductors and protective anodes, as packaging foils, and in composite products. Corrosion testing, therefore, is diversified and includes laboratory, field, and service requirements in natural as well as artificial environments. Typical tests range from stress corrosion methods to durability of coatings and include effects of antifoulants, heat treatments, anodized coatings, and weldments. Weathering characteristics are important for not only corrosion considerations but also for reasons of esthetics.

Many of the commonly used corrosion tests may be used for evaluation of any of the nonferrous metals. In addition, there are specialized tests for single alloy systems, in addition to those for different alloys within a system [1].

Listings of corrosion test specifications for individual metals and alloys are to be found in the series of Military Standardization Handbooks which include:

MIL-HDBK-694 (MR) Aluminum and Aluminum Alloys MIL-HDBK-698 (MR) Copper and Copper Alloys MIL-HDBK-693 (MR) Magnesium and Magnesium Alloys MIL-HDBK-697 (MR) Titanium and Titanium Alloys

An additional useful source of reference to specifications is Military Handbook MIL-HDBK-H1, "Cross Index of Chemically Equivalent Specifications and Identification Code (Ferrous and Nonferrous Alloys)." Included in this handbook are listings of specifications issued by the following agencies: General Services Administration (Federal); Department of Defense (MIL and JAN); American Iron and Steel Institute; Society of Aeronautical Engineers (AMS); Aluminum Association;

¹ Reynolds Metals Company, Richmond, Va.

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Society of Automotive Engineers (SAE); and American Society for Testing and Materials [2-6].

Standardization

The standardization of industrial corrosion test methods is accomplished through several channels. Trade associations for both nonferrous metal producers and users, professional organizations involving metallurgists and engineers, government and national standardization groups, and the International Standards Organization (ISO) are among those attempting to coordinate and establish acceptable and useful test methods. Such groups include the Aluminum Association (U.S.), the British Non-Ferrous Metals Research Association, the Aluminium Federation (British), the International Lead-Zinc Research Organization, the Copper Development Association, the American National Standards Institute, and the International Standards Institute.

Societies devoting strong leadership in the establishment of industrial corrosion standards are the American Society for Testing and Materials (Committee G-1 on Corrosion of Metals), the National Association of Corrosion Engineers, the American Electroplaters Society, and the Metal Properties Council (Subcommittee VIII on Corrosion).

Nonferrous Metals

Nonferrous metals include aluminum, copper, lead, magnesium, nickel, titanium, zinc, beryllium, and refractory materials, such as molybdenum, tantalum, and tungsten. In addition, certain metals are used for plating—among these are cadmium, chromium, tin, gold, and silver.

These nonferrous metals vary widely in chemical activity, from the generally active magnesium, aluminum, and zinc to the relatively inert, or passive, tantalum, silver, and gold. In addition to these differences, there are differences in activity among the alloys within a metal system such as aluminum.

Associated with the wide range of chemical activities for the nonferrous metals and alloys is a similar variation in corrosion resistances. The corrosion may take one or more forms of the following types of corrosive attack: uniform corrosion, pitting attack, intergranular attack, erosion corrosion, impingement attack, cavitation corrosion, fatigue corrosion, stress-corrosion cracking, filiform corrosion, dezincification, graphitization, fretting corrosion, high-temperature oxidation, biological attack, galvanic corrosion, and concentration-cell attack. These types of corrosion attack are discussed in Chapter 1 of this book [7–9].

The corrosion of nonferrous metals may be usefully grouped into the several metal systems. A discussion of a number of nonferrous metals and their alloys follows.

Aluminum

Although aluminum is one of the highly active metals, the normal oxide film present on the surface is relatively inert and acts as a corrosion barrier. When corrosion does occur on aluminum, the most common form is pitting attack, although a number of other forms may be present. The corrosion resistance of aluminum alloys varies considerably depending on the major alloying elements. Careful alloy selection and proper corrosion testing are essential, therefore, to insure satisfactory service life in a particular environment.

The designations of the various alloy groups under the Aluminum Association classification are associated with the major alloying elements and are shown in Table 1 (wrought alloys) and Table 2 (casting alloys).

		Alloy Number
Aluminum—99.00% minimum	and greater Major Alloying Element	1xxxª
Aluminum Alloys Grouped by Major Alloying Elements	Copper Manganese Silicon Magnesium Magnesium and Silicon Zinc Other Element	2xxx 3xxx 4xxx 5xxx 6xxx 7xxx 8xxx
Unused Series	Zinc Other Element	8 9

TABLE 1—Designations for wrought aluminum alloy groups.

^a The last two digits identify the aluminum alloy or indicate the aluminum purity. The second digit indicates modifications of the original alloy or impurity limits.

		Designation Number
Aluminum-99.00% r	ninimum and greater Major Alloying Element	1xx.x
Aluminum Alloys	Copper	2xx.x
Grouped by Major	Silicon, with added Copper and/or Magnesium	3xx.x
Alloying Element	Silicon	4xx.x
	Magnesium	5xx.x
	Zinc	7xx.x
	Tin	8xx.x
Unused Series		бхх.х
Other Major Alloying	Elements	9xx.x

TABLE 2—Designations for aluminum casting alloy groups.

Alloys having silicon, magnesium, or magnesium and silicon as major alloying elements have corrosion resistances ranking with that for pure aluminum.

The high-strength copper-bearing alloys may develop intergranular attack in corrosive environments, and stress-corrosion cracking may result from exposure of alloys having magnesium content in excess of 3.5 percent in severe environments.

Table 3 lists the corrosion resistances of many aluminum alloys and shows typical applications.

Resistance to Corrosion				
Alloy and Temper	Generalª	Stress Corrosion Cracking ^b	Typical Applications	
EC	A	A	Electrical Conductors	
1060	Α	A	Chemical Equipment, Railroad Tank Cars	
1100	Α	A	Sheet Metal Work, Spun Hollowware, Fin Stock	
2011-T3	D٥	D	Screw Machine Products	
T4. T451	Ď٥	D		
T8	$\tilde{\mathbf{D}}$	Ã		
2014-T3	D٥	Ĉ	Truck Frames, Aircraft Structures	
T6. T651	Ď	Ċ		
2017–T4	D°	С	Screw Machine Products Fittings	
2018-T61			Aircraft Engine Cylinders, Heads and Pistons	
2024–T4, T3	\mathbf{D}^{c}	С		
T361	D°	С	Truck Wheels	
T6	D	В	Screw Machine Products	
T861, T81, T8511	D	A	Aircraft Structures	
2025-T6	D	С	Forgings, Aircraft Propellers	
2117-T4	С	A		
2218-T61	D	С	Jet Engine Impellers and Rings	
2219-T31	D°	С	Structural Uses at High Temperatures (to	
T37	\mathbf{D}^{c}	С	600 F), High Strength Weldments	
T81	D	A		
T 87	D	A		
2618-T61	D	С	Aircraft Engines	
3003	Α	A	Cooking Utensils, Chemical Equipment, Pressure Vessels, Sheet Metal Work Builder's Hardware, Storage Tanks	
3004	Α	A	Sheet Metal Work, Storage Tanks	
4032–T6	С	В	Pistons	
5005	Α	A	Appliances, Utensils, Architectural, Electrical Conductor	
5050	Α	A	Builder's Hardware, Refrigerator Trim, Coiled Tubes	
5052	Α	A	Sheet Metal Work, Hydraulic Tube, Appliances	

 TABLE 3—Typical characteristics, applications, and resistance to corrosion of aluminum alloys.

Resistance to Corrosion Stress Corrosion Alloy and Temper General^a Cracking^b Typical Applications B^d 5056-0 \mathbf{A}^{d} Aď H111 B^d Cable Sheathing H12, H32 A^d B^d **Rivets for Magnesium** \mathbf{A}^{d} H14. H34 B^d Screen Wire H18, H38 Aď C^d Zippers A^d 5083 B^d Unfired, Welded Pressure Vessels 5086-0 A^d A^d Aď A^d H32 Marine, Auto Aircraft H34 A^d B^d Cryogenics, TV Towers H36 A^d B^d **Drilling Rigs** A^d \mathbb{R}^d Transportation Equipment, Missile Com-H38 ponents \mathbf{A}^{d} Welded Structures, Storage Tanks, Pressure A^d 5154 Vessels, Salt Water Service 5254 \mathbf{A}^{d} A^d Hydrogen Peroxide and Chemical Storage Vessels Automotive and Appliance Trim 5252 Α A Welded Structures, Pressure Vessels, 5454 Δ A Marine Service 5456 \mathbf{A}^{d} B^d High Strength Welded Structures, Storage Tanks, Pressure Vessels, Marine Applications 5457 A Α Hydrogen Peroxide and Chemical Storage 5652 Δ A Vessels Anodized Auto and Appliance Trim 5657 Α A 6053 А A Wire and Rod for Rivets В Heavy-Duty Structures Requiring Good 6061-0 A Т4 в В Corrosion Resistance, Truck and Marine, **T6** в A Railroad Cars, Furniture, Pipelines Pipe Railing, Furniture, Architectural 6063 Α A Extrusions

TABLE 3—Continued.

Copper

Copper and copper alloys are generally classed as being corrosion resistant. A surface coating or patina (basic copper sulfate and other compounds) protects the metal from further attack. Aqueous ammonia, solutions of cyanides, oxidizing salts and acids, and acids or salts in the presence of oxidizing agents prevent the formation of protective films.

Corrosion attack on copper and copper alloys may take the form of general corrosion, pitting, dezincification, stress corrosion, corrosion fatigue, and intercrystalline attack [6].

The groupings of copper and its alloys under the Copper Development Association system is shown in Table 4 [10].

		Stagen	
		Stress	
		Corrosion	m instanting
Alloy and Temper	Generala	Cracking	Typical Applications
6066–0	С	Α	Forgings and Extrusions for Welded
T 4	С	В	Structures
T 6	С	В	
6070	В	В	Heavy Duty Welded Structures, Pipelines
6101	Α	A	High Strength Bus Conductors
6151–T6, T652			Moderate Strength Intricate Forgings for Machine and Auto Parts
6201–T81	Α	A	High Strength Electric Conductor Wire
6262	В	Α	Screw Machine Products
6463	Α	A	Extruded Architectural and Trim Sections
7001	Cc	С	High Strength Structures
7039	В	С	Welded Cryogenic and Missile Applications
7075–0			
T 6	Cc	С	Aircraft and Other Structures
T73	С	Α	
7079-T6	Cc	Ċ	Structural Parts for Aircraft
7178–T6	C ^c	Ċ	Aircraft and Other Structures

TABLE 3—Continued.

^a Ratings A through E are relative ratings in decreasing order of merit, based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection. Alloys with C, D, and E ratings generally should be protected at least on faying surfaces.

^b Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5 percent sodium chloride alternate immersion test.

- A = No known instance of failure in service or in laboratory tests.
- B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens.
- C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens.
- D = Limited service failures with sustained longitudinal or long transverse stress.
- ^c In relatively thick sections the rating would be E.

^d This rating may be different for material held at elevated temperature for long periods.

For commercial pure copper small variations are not significant as to the corrosion resistance. Red brass is most corrosion-resistant of the brasses and resists dezincification and uncontaminated fresh waters. The bronzes are also strongly resistant to fresh water attack. Copper-tin and coppernickel alloys are very resistant to clean seawater. In contaminated seawater the cupro-nickel alloys, aluminum bronzes, and straight bronzes may be used. The 70-30 copper-nickel alloys resist stress-corrosion cracking and impingement attack.

Lead

Lead is corrosion resistant in hard and soft waters, most atmospheres and many chemicals. The protective coatings formed on lead are inert in many

Copper or Copper Alloy Number	Typical Alloy Number	Previous Trade Name	General Classification
100 to 150		Copper (99.3%)	Coppers
160 to 200	170, 172 175	Beryllium Copper (Cu 99.5%-Be 1.7) Beryllium Copper (Cu 99.5%-Co 2.5)	High Copper Alloys
200 to 300	210 220 230 240 260 280	Gilding, 95% Commercial Bronze, 90% Red Brass, 85% Low Brass, 80% Cartridge Brass, 70% Muntz Metal	Copper-Zinc Alloys (Brasses)
300 to 400	342	High-Leaded Brass	Copper-Zinc-Lead Alloys (Leaded Brasses)
400 to 500	465	Naval Brass, Arsenical	Copper-Zinc-Tin Alloys (Tin Brasses)
500 to 530	510	Phosphor Bronze, 5% (A)	Copper-Tin Alloys (Phosphor Bronzes)
530 to 645	614	Aluminum Bronze	Copper-Tin-Lead Alloys (Leaded Phosphor Bronzes)
645 to 665	655	High Silicon Bronze (A)	Copper-Silicon Alloys (Silicon Bronzes)
665 to 700	675	Manganese Bronze (A)	Miscellaneous Copper-Zinc Alloys
700 to 735		Copper Nickel (All Grades)	Copper-Nickel Alloys
735 to 800	745, 754, 770	Nickel Silver, 65–18	Copper-Nickel-Zinc Alloys (Nickel Silvers)

 TABLE 4—Designations for wrought copper alloys.

environments. Alkalies attack lead as do soils having organic acids from wood. Lead-tin coatings on steel are effective if bare points can be avoided. Table 5 lists some of the common commercial lead and lead alloys and their uses.

Alloy	Composition	Typical Uses	
Chemical Lead	99.90% min.	Chemical Industry	
Corroding Lead	99.73%	Batteries, paint, cable	
Calcium Lead	0.028 % calcium	Cable and pipe	
Antimony Lead	1-9% antimony	Cable and batteries	
Soft Solders	5-50 % tin	Solders	
Lead-base Babbitt	Antimony (10–15%)-tin (5–10%)	Bearings	
Type Metal	Antimony (4–16%)-tin (4–8%)	Туре	

TABLE 5—Designations for lead or lead alloys.

Magnesium

Magnesium is one of the very active metals. In most atmospheres, an oxide film formed on the surface protects the magnesium. This film tends to break down in salt environments [6].

Magnesium alloys are subject to general corrosion attack, pitting, stress corrosion, corrosion fatigue, galvanic corrosion, and intergranular attack. Pure magnesium has considerably better corrosion resistance than its alloys, but the alloys are stronger.

Atmospheric corrosion rates are determined by the alloying elements and the type of environment. High humidity intensifies the corrosion. All magnesium alloys corrode in seawater and, to a lesser extent, in fresh water. Table 6 gives typical magnesium alloys.

Designation	Forms Available	Main Alloying Elements
AM100A	Sand and mold castings	Al-10%, Mn-0.2% min.
AZ92A	Sand and mold castings	Al-9%, Zn-2%, Mn-0.2% min.
M1A	Extrusions	Mn-1.2% min.
AZ31B	Castings, sheet, extrusions	Al-3%, Zn-1%
HK31A	Sand castings and sheet	Th-3.3%, Zr-0.7%
ZE10	Sheet and plate	Zn-1.3%, rare earths—0.17%

TABLE 6--Typical magnesium alloys.

Nickel

Nickel and its alloys are very resistant to corrosion and oxidizing agents are necessary for corrosion to take place. Monel has excellent resistance to minerals, acids, and salts. Inconel is usually more resistant to atmospheres than Monel or nickel. Nickel is a common plating material for steels in atmospheric exposures. Nickel resists corrosion by all fresh waters but pits under barnacles in seawater. High nickel alloys may be subject to intergranular attack [6]. Common nickel alloys are listed in Table 7.

FABLE 7— <i>Typical</i>	nickel	alloys.
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Designation	Common Name	Main Constituents
	Commercial Nickel	99.50 Ni-0.25 Mn
"Duranickel" 301	Age Hardenable	99.50 Ni-0.20 Mn
Nickel 211	Manganese-Nickel	95.00 Ni-4.75 Mn
Nickel 213	Cast Nickel	95.00 Ni-1.6 Si-1.5 C
Hastellov D		82 Ni-9 Si-3 Cu
Monel 400		66 Ni-31.5 Cu-1.4 Fe
Inconel 600		76 Ni-16 Cr-7, 2 Fe
Hastellov F		47 Ni-22 Cr-17 Fe-6 Mo
Thum 98		55 Ni-28 Cr-8, 50 Mo-5, 5 Cu
Ni-O-Nel 825		42 Ni-22 Cr-30 Fe-3 Mo

Titanium

Titanium and its alloys exhibit excellent corrosion resistance in many atmospheres and waters. Generally, titanium is resistant to stress corrosion, erosion-corrosion, galvanic corrosion, and oxidation in many environments, including seawater [6].

This corrosion resistance is a result of the stable oxide film normally present on the titanium surface. The diffusion of the oxygen into the metal at high temperatures may cause embrittlement and corrosion of the metal. Titanium stress corrodes in a limited number of environments such as nitrogen tetroxide, hydrobromic acid, red fuming nitric acid, and chloride salts at high temperatures (260 C and above). Table 8 shows some common titanium alloys.

		Major	Alloying Elements	, %	
Designation	Fe ^a	Pd ^b	Alb	Sn ^b	V ^b
 Ti 35 A	0.12				•••
Ti 50 A	0.20				
Ti 65 A	0.25			• • •	
Ti 75 A	0.30			• • •	• • •
Ti-0. 20 Pd	0.25	0.15			
Ti-5 Al-2.5 Sn	0.50		4–6	2-3	
Ti-6 Al-4V	0.25	<i>.</i>	5.76-6.75		3.5-4.5

TABLE 8-Titanium and its alloys.

^a Maximum.

^b Nominal.

Zinc

Zinc is used in corrosion engineering largely as a structural material or as a coating material on steel or other metals. Here the protection is primarily galvanic in nature, with the zinc being anodic to iron, nickel, lead, tin, and copper. With aluminum, zinc can be either cathodic or anodic. In the case of magnesium, zinc is cathodic. Zinc is also commonly used as an anode material for cathodic protection of ships, pipelines, structures and so on.

The corrosion of zinc usually is uniform in nature—deep pitting is rare. The rate of attack on zinc in natural waters is increased by the presence of oxygen, carbon dioxide, aeration, high temperatures, and agitation. Between pH values of 7 and 12.5 corrosion of zinc is relatively low. Soft water is more corrosive than hard water and a lack of oxygen can initiate pitting. Some commercial zinc alloys are listed in Table 9 [6].

Beryllium

Beryllium has good resistance to water, particularly when the water is aerated and has a velocity of 5 to 8 fps. At temperatures of 260 C (500 F) or

		Impurity Cor	ntent, % max.	
ASTM Grade	Pb	Fe	Cd	Total
Special High Grade	0.006	0.005	0.004	0.010
High Grade	0.07	0.02	0.07	0.10
Intermediate	0.20	0.03	0.50	0.50
Brass Special	0.60	0.03	0.50	1.0
Selected	0.80	0.04	0.75	1.25
Prime Western	1.60	0.08		

TABLE 9—Common zinc alloys.

more and a water velocity of 27 fps, intergranular attack may develop. Pitting occurs in the presence of chloride ions [6].

Refractory Metals

Such metals as tungsten, tantalum, and molybdenum are used because of high structural strength at high temperatures. These metals are resistant to corrosion in many media at low temperatures and do not oxidize until a temperature of 300 C (572 F) or more is reached.

Discussion of Common Corrosion Tests

Laboratory Tests

Cabinet Tests

- 1. Neutral Salt Spray (ASTM B 117). Specimens are placed in a sealed cabinet having a 5 percent salt fog at 35 C. Now used for evaluation of painted, plated, and anodized parts.
- 2. Acidified Salt Spray (ASTM B 287). The pH of 3.2 is obtained by acidifying the fog solution of B 117 with acetic acid. For evaluation of organic and inorganic coatings, plated metal and anodized specimens. Also used for exfoliation testing of aluminum.
- 3. CASS Test (ASTM B 368). A 5-percent salt fog maintained at 49 C with a pH of 3.2 and made more aggressive by the addition of copper to the test solution. Primarily used for the testing of decorative copper-nickelchromium or nickel-chromium coatings on zinc-base die castings, anodized aluminum, and painted metals.
- 4. Corrodkote Test (ASTM B 380). A slurry containing corrosive salts is applied to test specimens and allowed to dry. Specimens are then placed in a high humidity cabinet at 38 C. Used for decorative chromium plating and stainless steels.
- 5. Kesternick Test (German Standard DIN 50018). Hot moist SO₂, followed by ambient air, is circulated at controlled temperature and humidity. Used for plated coatings and stainless steel fittings.

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- 6. Humidity Tests. Controlled high humidity (70 to 100 percent) at temperatures from ambient to 49 C. Used for organic and metallic coatings.
- 7. SWAAT Test (Reynolds Metals Company STP AC7). Cyclic acidified 3.5 percent salt spray. Used for exfoliation testing of aluminum.
- 8. Cargill Test. A test simulating road conditions and involving intermittent melting and cycling temperatures after application of a slurry on specimens.

Beaker Tests

- 1. Kape Test. An immersion test having a sodium sulfate-sulfuric acid solution at 95 C. Used for testing the sealing of anodized aluminum.
- 2. Dip and Dry Test. Alternate immersion of specimens in a corrosive solution. Solution may be 3 percent sodium chloride or salt solutions having sulfur compounds. Used for stainless steel materials.
- 3. Ferric Chloride Spot Test. A drop of FeCl₃-NaCl-HCl solution is placed on the cleaned metal surface. Used for stainless steels to indicate chromium depletion.

Electrochemical Tests

- 1. FACT Test (Ford Anodized Aluminum Corrosion Test). A technique where a d-c current passed through an acid salt solution on an anodized aluminum surface. The integral of the time-voltage breakdown curve is the FACT number.
- 2. AZTAC Test (Alcoa Impedance Test for Anodic Coatings). This test measures the a-c impedance of an anodic aluminum coat at a spot wetted with chloride solution.
- 3. EC Test (General Motors Electrolytic Corrosion Test). A potentiostatic test for chromium-nickel plating systems. The specimen is held at a potential of +0.3 V versus a saturated calomel electrode for 1 min, followed by free corrosion for 2 min.
- 4. Electrographic Printing Test. A paper sensitized with indicators for a certain metal is pressed on the specimen surface (anode) and a potential 1.5 to 6.0 V is applied. Colored spots on the paper indicate the presence of discontinuities in the coating.
- 5. Polarization Resistance Test (Linear polarization technique). Used for many systems, including pitting sensitivity of stainless steels.

Field Tests

Field tests are those tests carried out in natural environments of the types in which specimens are likely to be exposed. Field tests may be made in air, water, or soil [12].

Atmospheric specimens are most often of the panel type (for example, 4 by 6 in., 4 by 8 in., or 4 by 12 in.) and are supported at the edges by porcelain or plastic knobs. The usual exposure rack faces south and panels are exposed at 30 or 45 deg from the horizontal. Test racks should not be sheltered but should have a bold exposure free of local unusual air currents or corrosive effects. Since the time of initial exposure establishes the first surface film, it is important to make exposures on an annual basis at approximately the same time. Even in waters this can be important due to temperature effects.

Seawater exposures may be tidal (at the tidal zone), full immersion, or partially buried in the ocean bottom. Soil tests require extra care due to variations in soils and their air and water contents.

Service Tests

Service tests are tests involving actual components or assemblies in the field rather than panels. Presumably a better judgement as to the corrosion resistance of the test specimen is obtained in this fashion. However, more care may be required in planning and executing these tests than is needed for other methods [18].

APPENDIX

Corrosion Tests

Laboratory Corrosion Tests

American Society for Testing and Materials (ASTM)

- B 117 Salt Spray (Fog) Testing
- B 136 Test for Resistance of Anodically Coated Aluminum to Staining by Dyes
- B 137 Test for Weight of Coating on Anodically Coated Aluminum
- B 244 Measuring Thickness of Anodic Coatings on Aluminum with Eddy Current Instruments
- B 287 Acetic Acid Salt Spray (Fog) Testing
- B 356 Specification for Zirconium and Zirconium Alloy Forgings and Extrusions for Nuclear Applications
- B 368 Copper-Accelerated Acetic Acid Salt Spray (Fog) Testing (CASS Test)
- B 380 Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure
- B 449 Recommended Practice for Chromate Treatments on Aluminum
- C 464 Corrosion Effects of Thermal Insulating Cement on Base Metal
- C 486 Test for Spalling Resistance of Porcelain Enameled Aluminum
- D 69 Specification for Friction Tape for General Use for Electrical Purposes
- D 130 Test for Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test
- D 235 Specification for Petroleum Spirits (Mineral Spirits)
- D 801 Dipentene, Sampling and Testing
- D 807 Corrosivity Test of Industrial Water (USBM Embrittlement Detector Method)
- D 849 Test for Copper Corrosion of Industrial Aromatic Hydrocarbons
- D 930 Total Immersion Corrosion Test of Water-Soluble Aluminum Cleaners
- D 1141 Specification for Substitute Ocean Water (not a corrosion test but contains directions for preparing a corrodent)

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- D 1261 Test for Effect of Grease on Copper
- D 1275 Test for Corrosive Sulfur in Electrical Insulating Oils
- D 1280 Total Immersion Corrosion Test for Soak Tank Metal Cleaners
- D 1374 Aerated Total Immersion Test for Metal Cleaners
- D 1384 Corrosion Test for Engine Antifreezes in Glassware
- D 1567 Testing Detergent Cleaners for Evaluation of Corrosive Effects on Certain Porcelain Enamels
- D 1611 Test for Corrosion Produced by Leather in Contact with Metal
- D 1616 Test for Copper Corrosion by Mineral Spirits (Copper Strip Test)
- D 1654 Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
- D 1735 Water Fog Testing of Organic Coatings
- D 1743 Test for Rust Preventive Properties of Lubricating Greases
- D 1748 Test for Rust Protection by Metal Preservatives in the Humidity Cabinet
- D 1838 Test for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases
- D 1838 Test for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases
- D 2043 Test for Silver Tarnishing by Paper
- D 2251 Test for Metal Corrosion by Halogenated Organic Solvents and Their Admixtures
- D 2570 Simulated Service Corrosion Testing by Engine Antifreezes
- F 64 Test for Corrosive and Adhesive Effects of Gasket Materials on Metal Surfaces
- G 1 Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens
- G 2 Recommended Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys
- G 4 Recommended Practice for Conducting Plant Corrosion Tests
- G 28 Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys

Recommended Practice for Laboratory Immersion Corrosion Testing of Metals

- Recommended Practice for Recording Data from Atmospheric Corrosion Tests of Metallic-coated Steel Specimens
- Recommended Practice for the 3.5 percent Sodium Chloride Solution Alternate Immersion Stress-Corrosion Test (1)
- Method of Test for Exfoliation Corrosion Susceptibility in 7000 Series Copper Containing Aluminum Alloys

Federal Test Methods

Method 812	Synthetic Sea Water Spray Test
Method 822	Intergranular Corrosion Test for Aluminum Alloys
MIL-STD-171	Finishing of Metal and Wood Surfaces (for aluminum)
MIL-STD-186	Protective Finishing Systems for Rockets, Guided Missiles,
	Support Equipment and Related Materials
MIL-STD-193	Painting Procedures, Tactical Vehicles (Tracked and Wheeled)
MIL-STD-194	Painting and Finishing Systems for Fire Control Instruments
MIL-STD-276	Impregnation of Porous Nonferrous Metal Castings
MIL-T-152	Treatment, Moisture- and Fungus-Resistant, of Communica-
	tion, Electronic, and Associated Electrical Equipment
MIL-V-173	Varnish, Moisture- and Fungus-Resistant (for the treatment of
	Communications. Electronic, and Associated Electrical Equip-
	ment)
MIL-F-495	Finish, Chemical, Black, for Copper Alloys

MIL-M-3171	Magnesium Alloy; Processes for Corrosion, Protection of
MIL-C-5541	Chemical Films and Chemical Film Materials for Aluminum
	and Aluminum Alloys
MIL-S-7124	Sealing Compound, Pressure Cabin
MIL-F-7179	Finishes and Coatings; General Specifications for Protection of
	Aircraft and Aircraft Parts
MIL-P-8116	Putty, Zinc Chromate, General Purpose
MIL-P-8585	Zinc Chromate Primer (for aluminum)
MIL-A-8625	Anodic Coatings for Aluminum and Aluminum Alloys
MIL-C-8837	Coating Cadmium (Vacuum Deposited)
MIL-T-10727	Tin Plating; Electrodeposited or Hot Dipped for Ferrous and Nonferrous Metals
MIL-S-11031	Sealing Compound Noncuring Polysulfide Base
MIL-C-11796	Corrosion Preventive, Petrolatum, Hot Application
MIL-L-13762	Lead Allov Coating, Hot Dip (for Iron and Steel Parts)
MIL-L-13808	Lead Plating (Electrodenosited)
MIL-I-13857	Impregnation of Metal Castings
MIL-F-13924	Coating, Oxide, Black, for Ferrous Metals
MIL-F-14072	Finishes, for Ground Signal Equipment
MIL-P-14458	Paint, Rubber, Red Furning Nitric Acid Resistant
MIL-P-14538	Plating, Black Chromium (Electrodeposited)
MIL-C-14550	Copper Plating (Electrodeposited)
MIL-Z-17871	Zinc Coating (Hot Din Galvanizing)
MIL-P-23408	Plating Tin-Cadmium Electrodeposited
MIL-C-26074	Coating, Nickel-Phosphorus, Electroless Nickel, Requirements
	for
MIL-A-40147	Aluminum Coating (Hot Dip) for Ferrous Parts
MIL-M-45202	Magnesium Alloys, Anodic Treatment of
MIL-G-45204	Gold Plating (Electrodeposited)
MIL-P-45209	Palladium Plating (Electrodeposited)
MIL-A-46063	Aluminum Alloy Heat-treatable Armor Plate
MIL-C-46079	Coating, Epoxy, Baking Type for Magnesium Castings
MIL-M-46080	Magnesium Castings, Process for Anodic Cleaning and Surface
MIL-A-46118A	Aluminum Allov Armor Plate and Forgings 2219
MIL -C-60536	Hard Coat Anodize (for aluminum)
MIL -C-60539	Anodic Coatings for Aluminum
OO-C-320	Chromium Plating (Flectrodenosited)
00-P-416	Plating Cadmium (Electrodeposited)
00-N-290	Nickel Plating (Electrodeposited)
00-P-35	Passivation Treatments for Austenitic Ferritic and Martensitic
~~~~~	Corrosion-Resisting Steel (Fastening Devices)
QQ-S-365	Silver Plating, Electrodeposited: General Requirements for
00-Z-325	Zinc Coating, Electrodeposited, Requirements for
TT-C-520	Coating Underbody (for Motor Vehicles)
AMS 2468	Hard Coating Treatment of Aluminum Allovs
National Associat	ion of Corrosion Engineers (NACE)

National Association of Corrosion Engineers (NACE)

TM-01-69 Laboratory Corrosion Testing of Metals for the Process Industries

Corrosion Tests Not Issued by Any Standards Organization

FACT Test (Ford Anodized Aluminum Corrosion Test) Electrochemical Test in Acid Salt Solution for Evaluating Anodizing

SWAAT Test-Standard Method for Exfoliation Testing of Aluminum Alloys-

Reynolds Metals MRD-STP AC 7; Acid Seawater Spray 30 min; 100% RH, 90 min

- Ferric Sulfate—Sulfuric Acid Test for Ni-Cr-Mo Alloys. Quality Control and Acceptance Test for Satisfactory Heat Treatment
- Kesternich Test (German Standard DIN 50018) Hot Moist SO₂ followed by Ambient Conditions for Testing Metallic Protective Coatings
- Kape Test-Immersion in Acidified Sodium Sulfite for Testing the Sealing of Anodized Aluminum

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# Chapter 11

# Corrosion Standards and Control in the Iron and Steel Industry

H. P. Leckie¹

Corrosion testing in the steel producing industry is utilized to (a) provide a basis for internal quality control standards, (b) establish quality and performance parameters with respect to the final product utilization and (c) serve as a comparison standard in the development of new ferrous base products having improved corrosion resistance. The major markets served by the steel industry are automotive, construction, containers, rails, electrical, appliance and agriculture and both accelerated and field tests on steel products reflect the specific requirements in corrosion resistance properties for these industries. Any discussion of corrosion testing of steels must necessarily include coatings (both metallic and nonmetallic) since the shipped tonnages of coated steel products are large and continue to increase on a percentage basis year by year. Furthermore, although stainless and heat resisting steels represent less than one percent  $[1]^2$  of steel shipments in the United States, the more critical applications to which these materials are subjected, together with the specific forms of corrosion related failures experienced, warrant their inclusion in any description of the use of corrosion standards in the steel industry.

The widespread applications for steels and steel products are so diversified in scope as to require testing to determine resistance or susceptibility to generalized corrosion, localized (pitting) corrosion, stress corrosion cracking, hydrogen stress cracking, oxidation, galvanic corrosion and corrosion fatigue. On a more restricted basis there may also be the need to test for such forms of corrosion attack as graphitic, cavitation and fretting corrosion. For metallic coatings the corrosion resistance offered to the steel substrate depends primarily on thickness, and corrosion resistance is, therefore, often related indirectly to such factors as adhesion, ductility, hardness and porosity. Similar indirect corrosion testing is also applied to nonmetallic coatings. However, the situation with organic coatings differs from metallic corrosion testing in two major respects: (1) organic coatings are to

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² Italic numbers in brackets refer to references listed at the end of this chapter.

a greater or lesser degree permeable to moisture and (2) organic coatings are susceptible to degradation due to the action of ultraviolet light. As a result of either the separate or combined action of moisture and ultraviolet light, the physical properties of organic coatings may be changed in such a way (chalking, crazing, blistering, peeling, etc.) as to detract significantly from the corrosion resistance characteristics of the initially applied film.

Corrosion testing procedures for steels and steel products may be generally classified according to the three general categories of service, field and accelerated tests. Service tests refer to those conditions where a material is evaluated as to its performance as a specific end product in a specific in situ application. Corrosion service tests may involve the material under test experiencing the corrosive action of only one relatively uniform environment (for example, a domestic water tank) or varying environmental interactions (automobile body component). Field tests, on the other hand, are not normally conducted on finished component parts, but rather serve to gain general corrosion resistance information in the atmosphere, underground or under immersed conditions. Where field tests are conducted under immersed conditions, the environment must be and is always defined (for example, flowing sea water). For atmospheric corrosion field tests the necessity for describing local atmosphere conditions, while not as critical as the need for describing immersed conditions, nevertheless is most desirable. The atmospheric corrosion behavior of steels varies considerably with environment. Table 1, for example, shows the relative corrosivity of several atmospheric test site locations for mild steel.

Site	1 Year	2 Years	4 Years	8 Years
State College, Pa. (Rural)	1.0	1.0	1.0	1.0
South Bend, Pa. (Semi-Rural)	1.5	1.5	1.6	1.7
Kure Beach, N.C. (Marine)	2.0	2.5	3.5	5.8
Kearney, N.J. (Industrial)	3.3	2.7	2.5	2.6

TABLE 1-Relative corrosivity of atmospheric corrosion test sites.ª

^a State College, Pa. as unity.

Underground (soil) test conditions are specified with the least frequency, although the variations in soil characteristics with respect to pH, electrical resistivity, bacterial activity and composition are sufficient to cause significant variations (up to orders of magnitude) in corrosion rate for the same material. For this reason, the location, together with a general description of soil type, should always be specified in describing underground field corrosion test data.

In view of the great diversity of natural environmental conditions, the extrapolation of accelerated laboratory test data to predict corrosion per-
formance of a given material in service must be approached with great caution. Accelerated tests, by definition, are designed to represent conditions more severe than those normally encountered in service.

By using a control material of known corrosion resistance performance under real conditions, it is possible through judicious choice of the accelerated test procedure to gain comparative corrosion rate information on a relative basis. However, rather than specifying materials for service applications based on accelerated test data, accelerated tests are more commonly used in the steel industry either as quality control procedures or as means for evaluating the relative corrosion resistance of materials in the area of new product development.

To the best of the writer's knowledge, one of the first published procedures for accelerated testing designed to simulate atmospheric corrosion behavior was described by Capp [2] in 1914. Most of the now widely accepted humidity and salt spray test methods derive from variations and improvements on this early work. The importance of such variables as relative humidity, temperature, and contaminants on the atmospheric corrosion behavior of both ferrous and nonferrous metals was first described in detail by Vernon [3-6]. An early humidity cabinet designed to provide continuous condensation on test specimens was developed and described by Darsey [7]. Various procedures were developed [8-11] which allowed test specimens within a cabinet to be physically rotated through various locations having different humidity-temperature conditions, and in this manner simulate more closely real atmospheric exposure conditions. Other variations [12-14] alternately changed conditions within the test cabinet so as to permit condensation to occur during specified portions of the test cycle. The use of sprays and fogs particularly from salt solutions was first described in 1937 [15] and modification and upgrading continues to the present day. A tentative procedure for salt fog testing was first published by the American Society for Testing and Materials (ASTM) in 1939 followed by revisions in 1941, 1944, 1949, 1954, 1957, 1961, and 1964. The most recent revision is designated ASTM B 117-64. Variations on the salt fog test procedure involving pH control using acetic acid and the additicn of copper chloride to increase aggressiveness of the fog, carry the designations ASTM B 287-62 and ASTM B 368-68, respectively. The deficiencies in attempting to correlate accelerated corrosion tests with atmospheric corrosion behavior for steels and coated steels is well recognized and were briefly described earlier. Some of the deficiencies in accelerated test procedures have been detailed by Schlossberg [16]. A literature survey by Kuensler and Shur [17] covering the period 1956 to 1966 covers the accelerated testing of organic coatings with respect to weathering resistance.

It is now generally accepted that the single factor contributing most to variations in atmospheric corrosion behavior is the concentration of sulfur dioxide [18]. Testing in SO₂ atmospheres, although reported much earlier,

did not gain wide acceptance until the apparatus developed by Kesternich [19] was described in 1951. This equipment combined exposure to  $SO_2$  together with continuous condensation on the surface of the test specimens. More recent work [20-30] attests to the use of continuous condensing systems containing  $SO_2$  as providing reasonably close correlation between an accelerated corrosion test procedure and atmospheric corrosion behavior in an industrial environment.

For convenience in presentation, specifics of corrosion and corrosion testing in the iron and steel industry will be discussed under various materials categories.

### **Plain Carbon and Low-Alloy Steels**

The corrosion of carbon and low-alloy steels is primarily governed in most cases by the combined action of water and oxygen. Under most conditions of natural corrosion, the rate is controlled by the cathodic reaction (normally oxygen reduction) which explains the relatively minor effect of small alloying additions on the corrosion rate of iron. In simple terms, the corrosion of iron may be characterized by the following chemical reactions:

$$2 \operatorname{Fe} + 2 \operatorname{H}_2 \operatorname{O} + \operatorname{O}_2 \to 2 \operatorname{Fe} (\operatorname{OH})_2 \tag{1}$$

4 Fe (OH)₂ + 2 H₂O + O₂ 
$$\rightarrow$$
 4 Fe (OH)₃ (2)

In practice rust films on iron and steel generally comprise several layers, representing iron oxides in various states of oxidation. A recent publication by Evans and Taylor [31] details the chemistry of the atmospheric rusting of iron.

Under immersed conditions the corrosion of iron may or may not be primarily controlled by the cathodic reduction of oxygen. In acid solutions the reduction of hydrogen ions at cathodic sites becomes the rate controlling process. In actual practice a combination of both oxygen and hydrogen ion reduction takes place. As a guideline, it may be considered that over the pH range 4 to 10 the corrosion rate of iron is essentially unaffected by pH and is controlled by the diffusion rate of oxygen to the metal surface. In this region the corrosion product film is ferrous hydroxide (hydrated ferrous oxide) producing an effective pH at the iron-ferrous hydroxide interface of approximately 9.5. At pH <4 ferrous hydroxide is unstable and the corrosion rate rises rapidly with decreasing pH. At the lower end of the pH scale, surface coverage by hydrogen approaches unity and the corrosion rate is controlled by the rate of hydrogen evolution. In highly alkaline solutions (pH >10) iron is passive and the corrosion rate is correspondingly reduced. Concentrated alkaline solutions (pH > 14) cause iron to dissolve as the ferrite (FeO₂⁻) anion, although the kinetics of reaction are so slow as to produce only a very minor increase in corrosion rate over passive iron. Salt tends to increase corrosion rate due to a combination of increased electrolytic conductivity of the solution and the formation of nonprotective corrosion products at some location removed from the iron surface [32]. Certain oxidizing ions readily reducible at cathodic sites (ferric, cupric, mercuric) may also stimulate the overall corrosion rate significantly, due to their depolarizing action on the cathodic reaction kinetics.

Under conditions of oxygen reduction, as the controlling cathodic reaction, the effects of coldwork and small amounts of alloying additions on corrosion rate are minimal. In acid solutions, however, a small but apparently real effect for coldwork in increasing the corrosion rate of iron in acid solutions has been reported [33] due to the formation of finely dispersed low overvoltage areas of nitride and carbide precipitates. Similarly, heat treatment to the extent that it may vary the volume fraction of low overvoltage iron carbide may also affect the corrosion rate of iron in acid solutions.

Although it has previously been stated that the corrosion rate of iron under conditions of oxygen reduction as the primary cathodic reaction is relatively unaffected by additions of small amounts of alloying elements, the composition and protectiveness of the corrosion product film is indeed affected by steel composition, particularly under atmospheric but also to a lesser extent under immersed exposure conditions. The ability of copper to retard corrosion in iron and steel for instance was first reported in 1900 [34]. Howe [35] showed as early as 1901 that a 3-percent nickel steel corrodes at a substantially lower rate in the atmosphere than unalloyed steels. The effect of alloying additions on the corrosion resistance of iron and steel has been studied extensively since that time [36-53]. (The list of references given here is intended to be representative and is by no means exhaustive.) The earliest extensive atmospheric exposure tests of various ferrous materials were started by ASTM in 1916-the final report on this investigation being published in 1953 [48]. This study showed that both copper and phosphorus contributed significantly to enhance corrosion resistance. Greenidge and Lorig [42] published the results of a three-year atmospheric corrosion program test on 43 steels which indicated that copper at levels between 0.2 and 0.5 percent markedly improved the corrosion resistance of low-carbon and low-alloy steels. Higher levels of copper did not appear to increase the resistance substantially. They concluded that 0.4 percent nickel added to copper steels is not very effective, but Pilling and Wesley [43] showed that a nickel addition of 2 percent results in a marked improvement. Sims and Boulger reported in 1944 [45] that the addition of 2 percent nickel was less effective than much smaller additions of phosphorus. In 1948, Pilling and Wesley [46] reported that phosphorus and silicon additions to copper-nickel steels were beneficial, but that carbon and manganese were unimportant in an industrial atmosphere. In 1952, Copson [47] reported the results of 9-year exposure of 71 low alloy steels at Bayonne, New Jersey, and Block Island, Rhode Island. This data confirmed the beneficial effect of fractional

percentages of copper, of small amounts of phosphorus, and of 1 percent or more nickel. Chromium and copper additions to complex steels were seen to be more helpful in the industrial atmosphere at Bayonne, whereas manganese appeared to be more helpful in the marine atmosphere at Block Island. Hudson and Stanners in 1955 [49] reported that the most useful alloying elements for the purpose of enhancing atmospheric corrosion resistance are chromium, copper, and nickel. They indicated that aluminum and beryllium might also be of value. Larrabee and Coburn in 1961 [51] reported corrosion data on 270 steels with systematic variations of copper, nickel, chromium, silicon, and phosphorus after exposure for 15.5 years in an industrial, a semirural, and a marine atmosphere. This work indicated that although an improvement in corrosion resistance can be obtained by relatively small additions of these elements singly, the greatest improvement derives from interactions between specific combinations of these alloying additives. Wiester and Ternes [52], who reviewed the development of low alloy steels for atmospheric corrosion resistance, concluded that copper, phosphorus, chromium, nickel, and molybdenum were the additives sufficiently effective in this regard to warrant singling out.

In summary, over the years at least eleven elements have been reported as contributing to corrosion resistance in low-alloy steels: aluminum, antimony, beryllium, chromium, copper, manganese, molybdenum, nickel, phosphorus, silicon, and titanium. A full factorial experimental design for this many additives at only one concentration level would require the preparation and processing of 211 or 2048 alloys, and this would allow for no variation in preparation or processing. The establishement of nonlinear effects would require the preparation of a significantly greater number of experimental compositions. A method of avoiding the complete factorial experiment in producing compositions for alloy development when the number of variables to be considered is impractically large has been suggested by Plackett and Burman [54]. This experimental design makes possible the determination of main effects from data obtained in a minimum number of experiments. For eleven variables, for example, main effects can be determined from twelve experiments. A Plackett-Burman design can thus be used as a screening procedure to identify the most promising additives with respect to corrosion resistance which can subsequently be examined for interactions in a conventional factorial design. Multiple regression analysis can then be used to determine a mathematical relationship between atmospheric corrosion rate and alloy additive concentrations which may be used for predictive purposes.

The most commonly quoted elements for improving the atmospheric corrosion resistance of low-alloy steels are copper, phosphorus, chromium nickel, molybdenum and to a lesser extent silicon. From these additives was developed a series of low-alloy steel compositions commonly known as the "weathering" steels, having corrosion resistance up to six times that of



FIG. 1—Atmospheric exposure weight gain versus time for weathering steel, mild steel and copper-bearing steel.

plain carbon steel in many atmospheric test locations. Typical weight-gain versus time curves for a weathering steel compared to mild steel and copperbearing steel are shown in Fig. 1.

Laboratory accelerated tests designed to predict atmospheric corrosion performance for low-alloy steels have for the most part been ineffective. Initial tests attempted to correlate atmospheric exposure rate with weightloss measurements obtained in 20 percent sulfuric acid [55]. It was recognized early [56], however, that the atmospheric corrosion rate of low-alloy steels was affected more by the protective qualities of the rust film than inherent corrosion rate of the bare steel. While it has been observed that certain accelerated tests involving exposure to sprayed solutions of various kinds and to moist sulfur dioxide correlate qualitatively with the observed corrosion rates of selected low-alloy steels in certain atmospheres, there has been no great success in demonstrating the observed beneficial contributions of specific alloying elements using accelerated tests.

Pourbaix [57] has recently attempted to predict weathering characteristics of low alloy steels from their potential/time behavior in an alternating immersion dry test. It is claimed that those alloys showing a propensity for the formation of protective "patinable" rust films exhibit a rapid rise in potential (see Fig. 2) in the noble direction to a value approximately 200 mV more noble than the "non-patinable" steels which exhibit a much reduced rate of potential increase. It was also demonstrated in these experiments that steel surface preparation was an important factor in the rate of formation of protective rust films. The potential/time data obtained by Pourbaix would indicate that a protective patina forms more rapidly on pickled rather than sand-blasted surfaces.



FIG. 2—Potential time behavior for patinable and nonpatinable steels.

Matsushima and Ueno [58] showed that the protective rust films formed on low-alloy weathering steels exhibited less "active corrosion sites" than plain carbon steels exposed for a similar duration in the atmosphere. Active corrosion sites were identified using an autoradiographic technique in which samples of steels corroded for various lengths of time in the atmosphere were immersed in a sodium sulfate solution containing radioactive  $SO_4^{--}$  and subsequently placed on an X-ray film. These authors explained the increased corrosion resistance of weathering steels on the reduced tendency for their rust films to catalyze the conversion of  $SO_2$  to  $SO_3$  and to the more continuous nature of the rust coating which is reflected in an increased anodic polarization.

In general, immersed electrochemical test procedures have been singularly unsuccessful in predicting even relative corrosion rates of carbon and low alloy steels in the atmosphere. This is again due to the fact that immersed exposure conditions do not produce the same physical and chemical properties of the rust films formed on the same steel compositions under atmospheric exposure conditions. Electrochemical test procedures have, on the other hand, shown reasonable correlation with observed corrosion rates in specific environments under immersed conditions. Thus, Cohen and Jelinek [59] obtained good correlation between the corrosion rate measured directly by weight loss and indirectly from the linear polarization method for the corrosion of mild steel in alkaline lithium bromide solutions. Linear polarization resistance is obtained from the slope of the linear portion of a polarization curve measured at a potential range close (usually 5 to 10 mV) to the corrosion potential. The method has been demonstrated as applicable to the measurement of corrosion rate in a series of diverse real environments [60-65]. Anomalous data may be obtained, however, where more than one electrochemical oxidation reaction is proceeding simultaneously and, in particular, where such reactions do not involve metal dissolution.

### Metallic Coatings for Steel

Metallic coatings are applied to low-carbon steels primarily to effect an improvement in corrosion resistance, oxidation resistance and to a lesser extent for aesthetic purposes. Zinc and tin remain by far the most widely used coating materials, the former being applied by hot dipping and finding primary utilization as galvanized steel in the automotive industry. Production of hot-dip galvanized sheet and strip steel in the United States exceeded five million tons during the year 1970 [1]. Uses for galvanized steel other than for automotive applications include major appliances, construction and drainage products. Although the greatest tonnage by far of zinc-coated steel is produced by hot dipping, significant tonnages of steel are electroplated with zinc, producing what is commonly referred to as electrogalvanized steel. The corrosion resistances afforded by the two application methods are essentially the same, with total corrosion resistance being a direct function of the zinc coating weight. Hot-dip zinc coatings are produced to several standard coating weights, with coating weight control on continuous galvanizing facilities being achieved through gas impingement. ASTM Standard A 525 specifies the coating designation numbers

under which zinc coating weights on sheet steel are specified. The most commonly produced material, G.90, has a total coating weight (both sides) of 1.25 oz zinc/ft² with minimum check limit (triple spot test) of 0.90  $oz/ft^2$ . In like manner, galvanized sheet steel having the designation G.60 corresponds to a minimum coating zinc weight of 0.60 oz/ft². In 1971, the designation G.01 was introduced referring to extremely light hot-dip zinc coatings close to those produced during continuous electrogalvanizing in which no minimum coating weight is specified. Galvanized sheet steel is produced in four basic forms, as follows: (1) regular (or full) spangleproduced on continuous coating lines such that the surface exhibits the well-known "flowery" dendritic spangle; (2) minimized spangle-elimination of the spangle by modifying the nucleating characteristics of the coating during solidification; (3) iron-zinc alloy-a nonspangled matte finish suitable for painting, produced by processing the galvanized steel at sufficiently high temperatures to cause increased alloying; and (4) differential-galvanized steel having a specified zinc coating weight on one side and a significantly lighter zinc coating weight on the other side of the steel strip.

It was previously mentioned that the corrosion protection afforded by zinc coatings is a direct function of coating weight and this is attested to by the observed linearity in corrosion rate obtained during the atmospheric exposure of galvanized steel. Figure 3 shows the corrosion rate expressed as total weight loss in 4 by 6-inch test panels for commercial galvanized steel exposed for 6 years at a semi-industrial atmospheric corrosion test site in Porter County, Indiana. The data shown in Fig. 3 correspond to an annual loss in thickness of approximately 0.045 mil and thus, for a standard 1.25 oz/ft² coating (G.90) having a specified minimum zinc coating thickness of  $\sim 0.7$  mil, the first sign of red rust due to complete removal of the zinc coating might be expected in 15 to 16 years. This calculation, however, assumes uniform removal without preferential localized attack and applies to one environmental (semirural) test location only. A similar calculation for a more industrial atmospheric test site shows a corrosion rate for galvanized steel of 0.07 mil/year resulting in a predicted life for a G.90 coating of only 10 years. It should be pointed out, however, that nonuniform attack at coating defects will generally reduce the predicted life based on uniform attack assumptions.

In spite of the fact that zinc is electrochemically more active than iron, a comparison plot of atmospheric corrosion rates shows bare steel to corrode at a much higher rate than a galvanized coating, indicating that the zinc corrosion products offer a contribution to the retardation of corrosion rate by slowing the dissolution kinetics. In contrast to the uniform corrosion rate with time observed for zinc, bare low-carbon and alloy steels exhibit a pronounced reduction in rate with time. However, even after years the corrosion rate of bare steel exceeds that of the zinc coating by one order of



FIG. 3—Atmospheric exposure weight loss for galvanized steel exposed six years in Porter County, Indiana.

magnitude. This effect is shown in Fig. 4 for galvanized steel and a copperbearing uncoated steel exposed at Porter County, Indiana for 6 and 8 years, respectively, with exposure for both commencing in October 1963.

Since 1926, ASTM Committee A-5 has coordinated an atmospheric corrosion test program on corrugated galvanized sheets at five different test locations in the United States [66]. A second program undertaken by Subcommittee XIV of ASTM Committee A-5 to evaluate the atmospheric corrosion resistance of galvanized steel produced both by batch and continuous dipping techniques was initiated in 1960. Test samples were exposed at State College, Pennsylvania (rural), Newark, New Jersey (industrial), Kure Beach, North Carolina (marine), Brazos River, Texas (marine), and



FIG. 4—Comparative atmospheric exposure weight loss for galvanized steel and uncoated copper-bearing steel in Porter County, Indiana.

Point Reyes, California (marine). Hudson and Stanners [67] reported on a 12-year test program for various types of zinc-coated steel exposed to various British and tropical environments and again concluded that the life of a zinc coating in a given environment is a direct linear function of thickness.

In addition to the economic attractiveness of zinc as a coating for extending the usable life of steel, a further advantage is derived from the sacrificial action afforded by zinc to the steel substrate at cut edges, scratches and coating discontinuities in general. Under all conditions of atmospheric exposure, zinc has been found to be anodic to iron [68]. Protection of the steel base at such discontinuities is achieved both by the preferential dissolution of the zinc in the zinc-iron cell and the deposition of zinc corrosion products which further stifle the reaction. An excellent survey of the corrosion behavior of galvanized steel is contained in the Zinc Development Association publication, *Zinc: Its Corrosion Resistance*, by Slunder and Boyd [69].

Under immersed conditions zinc coatings continue to afford sacrificial protection to the base steel substrate, although ready removal of nonadherent zinc corrosion products results in a continued high dissolution rate of the zinc coating. Furthermore, it was first reported by Schikorr [70] that in various hot aqueous solutions a reversal in polarity between zinc and iron occurs such that the zinc may become cathodic to the steel. It should be emphasized that both temperature and solution composition are contributing factors to the potential reversal. This phenomenon has been the subject of intensive study due to the widespread use of hot-dip galvanized steel in domestic hot water systems.

Salt spray testing (ASTM B 117) is widely used as a quality control criterion in evaluating the corrosion resistance of zinc coatings. A common acceptance criterion for standard 11/4 oz/ft² (G.90) galvanized sheet steel in certain segments of the automotive industry is 240 h exposure to salt spray without the occurrence of red rust. For lighter coating weight, hot-dip or electrogalvanized steel and depending on the application of the fabricated component, salt spray life requirements may be specified at times considerably less than 240 h. The Preece test (ASTM A 239) is widely used as a control in establishing uniformity of zinc coatings on steel. Test panels are subjected to immersion in a copper sulfate solution for periods of 1 min and the total number of dips required to dissolve the zinc coating and deposit an adherent layer of copper over a specified area of the steel substrate is determined. The test is used primarily to determine the thinnest portions of the coating and finds widespread utilization for quality control in such critical materials applications as electrical raceways. The Kesternich SO₂-humidity test also provides a means for accelerated testing of galvanized coatings, and in addition may be used to demonstrate the effective sacrificial protection afforded by zinc at scribes and cut edges.

Hot-dip aluminized steel is produced on continuous coating lines by a limited number of steel companies in the United States. Hot-dip aluminum coatings are generally used where oxidation resistance is a requirement at temperatures to  $\sim 1250$  deg F in such applications as oven construction, heat shields and automotive exhaust system components. Silicon ( $\sim 10$ percent) is normally added to the molten aluminum bath in order to reduce the thickness of the brittle iron-aluminum alloy layer which forms at the steel-coating interface. Silicon also reduces the viscosity of the bath and results in a lighter coating than that produced from the "pure" aluminum bath. Silicon-free hot-dip aluminum coatings are also applied to steel for atmospheric corrosion resistance, although the utilization of the straight aluminum coating is significantly less than for the aluminum-silicon alloy coating. The aluminum-silicon alloy coating carries the ASTM designation Type I and is specified as containing silicon in the range of 5 to 11 percent. Further designation according to coating weight recognizes two classes, T1 40 (regular) and T1 25 (light) having minimum coating weights (triple spot test both sides) of 0.40 and 0.25 oz/ft², respectively, according to ASTM standard A 463-69.

Although having good atmospheric corrosion resistance, the Type I aluminum coating is not generally recommended for bold exposure applications for aesthetic reasons, in that the silicon in the coating tends to impart a dark grey-black stain on exposure to many environments. At the present time, there is no ASTM designation for the unalloyed aluminum coating which is used in outdoor atmospheric exposure applications such as farm

silos and metal building roof decks. In general, for equivalent coating thicknesses the atmospheric corrosion rate of aluminized coatings are approximately one-third those of galvanized coatings. However, the sensitivity of aluminum coatings to the nature of environment is significantly greater than for galvanized coatings and probably relates both to the active-passive behavior of aluminum and the polarity reversals with steel which occur in a number of environments. For example, in a 3-year test conducted at a semiindustrial atmospheric corrosion test site in Porter County, Indiana, aluminized steel showed a pronounced increased corrosion resistance over galvanized steel (0.016 mpy versus 0.049 mpy), while the same materials tested in the highly industrial environment (HCl fumes) of a chemical plant in the Gulf area of Texas exhibited essentially reverse behavior.

Under immersed conditions, aluminum generally exhibits a potential noble to steel resulting in accelerated attack on the steel base at discontinuities in the coating. In environments containing ions conducive to the breakdown of passivity (Cl⁻, deaerated  $SO_4^-$ ) the potential of the aluminum coating becomes more active than that of iron and under these conditions cathodically protects the steel substrate by sacrificial action.

For a holiday-free aluminum coating, extremely long salt fog life, in the range of 500 to 1500 hours, is obtained prior to the incidence of red rust. At the present time there is no ASTM test procedure for measuring uniformity and thickness of aluminized coatings, although some consideration has been given to a test similar to the Preece test for galvanized coatings. The test consists of repeated immersion in a solution containing copper and fluoride ions in the presence of sulfuric acid. As with the Preece test, the number of dips required to expose the steel substrate and deposit a layer of adherent copper is determined.

A test developed for determining coverage of aluminum coatings involves immersion in a 35-percent nitric acid solution at room temperature and measuring the quantity of hydrogen produced by reaction of the acid with exposed areas of bare steel.

Tin-coated steel (tin plate) represents one of the major products of the steel industry accounting for approximately 5.7 million tons of steel shipped during the year 1970 [1]. Prior to 1937 all tin plate produced was manufactured by a hot-dipping process similar to that presently used for the continuous zinc and aluminum coating of steel. Today, essentially all tin plate is produced on continuous electrodeposition lines and the product is generally referred to as electrolytic tin plate.

The electrochemical sensitivity of tin-steel couples to the composition of the environment is very critical and tin may act either as a noble or a sacrificial coating. On exposure to the atmosphere and most aerated solutions, tin is noble with respect to steel and would tend to promote corrosion of the steel substrate at discontinuities in the coating. However, in the absence of air (food container applications) tin is almost always anodic to steel. The reversal in polarity is further promoted due to the complexing of stannous ions by many food products which results in a shift in the equilibrium potential for tin in the active direction due to the decreased activity of stannous ions. Furthermore, although dissolution of tin occurs in food product and beverage environments, the lack of toxicity of tin salts provides tin coatings with the required properties for can linings. In certain food product environments the dissolved tin salts may themselves act as inhibitors, thus decreasing the subsequent dissolution rate of the tin coating.

It was established many years ago that the composition of the base steel has a significant effect on the corrosion behavior of tin plate [71-73]. Phosphorus and silicon and in certain cases copper have been shown to be detrimental with respect to corrosion resistance, and for this reason these elements are normally specified to a minimum level. Corrosion of food and beverage cans manufactured from tin plate may occur by reaction with the atmosphere prior to filling the container, by chemical reaction with the alloy coatings for certain specific corrosion resistance applications. Such coatings normally contain 10 to 25 percent tin and the coated steel product is known as terne plate. Terne plate has a cost advantage over tin plate and in addition is more readily drawn, stamped and soldered. The primary disadvantages of the coating are unattractive appearance and unsuitability for contact with foodstuffs and beverages due to the toxicity of lead.

Although other metal coatings (nickel, cadmium, chromium) are applied to steel for improved corrosion resistance, only insignificant quantities are produced as primary steel industry products and, therefore, will not be considered here.

### **Organic Coatings for Steel**

In 1971, approximately 1.25 million tons of precoated painted steel strip were consumed in North America, and according to statistics supplied by the National Coil Coaters Association production since 1962 has increased at an average annual rate of  $\sim 18$  percent. Although large quantities of prefabricated structural and sheet steel are painted in the field, the present section will be restricted to a discussion of precoated strip since in many cases this is a basic product produced within the steel industry.

The continuous painting of steel (galvanized steel, aluminum) strip is referred to as coil coating. At the present time, most coil coated steel finds application in the construction market primarily for pre-engineered steel buildings. This market is followed in size by those of container and packaging products. It is anticipated that the major growth areas for coil-coated steel in the near future will be in the automotive and appliance industries.

On a modern continuous coil coating line the steel strip is cleaned and pretreated followed by the application of a primer and top coat each of which is cured at a specified temperature range. A typical coil coating finishing system for galvanized steel building panels might consist of the

	Fluorocarbon	Silicone Polyesters	Polyesters	Acrylics	Vinyls	Alkyds
Acid Resistance Alkali Resistance Solvent Resistance Erosion Chalk Fade General Corrosion Resistance	Excellent Excellent Excellent Excellent Excellent Excellent Excellent	Excellent Good to Excellent Good to Excellent Excellent Excellent Excellent Good to Excellent	Good to Excellent Good to Excellent Good to Excellent Good Good Good	Good to Excellent Good to Excellent Excellent Fair to Good Fair to Good Fair to Good Fair to Good	Excellent Excellent Poor to Fair Fair to Good Fair to Good Fair to Good Good	Excellent Fair to Good Good Fair to Good Fair to Good Fair to Good Fair to Good Fair to Good Good

TABLE 2—Some comparisons of chemical and physical properties of selected generic-organic coating systems.

following sequence: (1) zinc phosphate conversion coating, (2) 0.2-mil epoxy primer with appropriate corrosion inhibitors added, and (3) 0.8-mil, silicone modified polyester top coat. Many coil coating lines also have facilities for applying organic coatings as laminates; the most common systems applied in this fashion are polyethylene, polyvinyl chloride and various copolymers of polyethylene with acetic acid and vinyl acetate. Generic organic systems commonly applied to cold-rolled and galvanized sheet strip include fluorocarbons, silicone polyesters, polyesters, acrylics, vinyls, urethanes, and alkyds. Specific mechanical and chemical properties requirements often require combining two or more of the above in one formulation. Table 2 outlines the relative properties of various organic systems.

Accelerated corrosion testing of precoated steel falls into the two general categories of accelerated chemical resistance testing and accelerated weathering testing. The former varies according to end use and includes, for example, salt fog testing for pre-primed automotive stock and SO₂-humidity tests for industrial building siding. Water, whether as a vapor, liquid, or solution, is the most universal chemical involved in the degradation or organic coatings [74] and several standard tests are in existence designed to evaluate resistance to water vapor and liquid in the atmosphere [74]. ASTM standard E 96 is the general technique for measuring water vapor permeability through organic films in sheet form, while ASTM Standard D 1653 is used to determine water vapor permeability of organic coatings. The most widely used test for measurement of resistance to water condensation utilizes the Cleveland Condensation Tester (ASTM Standard D 2247) in which coated test panels are subjected to continuous water vapor condensation at elevated temperatures. Coil coatings are normally evaluated at 60 deg C for periods ranging from 6 to 240 h.

Spot tests for determining resistance to specific environments include such specifications as ASTM Standard D 1303 (Household Chemicals) and ASTM Standard D 1540 (Transportation Industry), the latter including the effect of such chemicals as anti-freeze, lubricating oils, hydraulic fluids and polishing creams and waxes.

For outdoor exposed applications the only truly reliable test for organic coated steels is exposure under actual conditions of use. Guidelines for conducting exterior exposure tests to determine the service life of organic finishes are presented in the National Coil Coaters Association (NCCA) Technical Bulletin No. 111. ASTM Standards D 609 and D 823 describe the configurations and preparation of organic-coated test panels for both outdoor weathering and accelerated testing procedures.

Procedures designed to simulate natural outdoor weathering have been available for many years. In general, the devices used employ a high intensity ultraviolet light source and some form of either constant or cyclic temperature control. More recent devices incorporate humidity control, water sprays, and additives designed to simulate atmospheric pollution (for example, SO₂, CO, NO₂) [75]. Accelerated weathering tests of this type enjoy a mixed reputation as to the correlation obtained with natural outdoor weathering [76,77]. To a large extent the degree to which artificial weathering machines are useful in predicting actual service performance depends to a large extent on how closely the spectrum of ultraviolet light source approximates that of the solar spectrum. Various complex light-dark, wet-dry and contaminant-no contaminant combinations of cyles can now be programmed into the control systems of modern artificial weathering machines. ASTM Recommended Practices E 42 and E 239 cover operation of carbon arc and water cooled xenon arc-type weathering machines, respectively. In general, however, weathering machines are not to be recommended for comparing organic coatings based on different polymers (for example, acrylic versus polyester). General descriptions of these various testing procedures, together with more detailed descriptions of paint evaluation methods not covered by ASTM standards, are provided in the extensive Gardner-Sward Paint Testing Manual [78].

Infrared analysis is gaining in acceptance as a quality control tool in the identification and "fingerprinting" of paint formulations and is now being routinely used as a first-step check in the determination of deviation from formulation in paint failure analysis. The advent of Fourier Transform Spectroscopy (FTS) permits not only the establishment of more rapid and accurate infrared spectra, but by interfacing with a computer data bank containing standard spectra will allow an almost instantaneous determination of quantitative deviations from a given formulation.

Evaporative Rate Analysis (ERA) continues to gain wider utilization as a means of investigating such parameters as surface cleanliness, degree of cure or cross-linking of adhesives and organic coatings, modifier migration and film forming. ERA involves measurement of the rate of evaporation or desorption of a minute amount of radioactive high boiling point material (for instance, tetrabromoethane C14) which is deposited on the surface being investigated. The rate of desorption is a reverse function of the "activity" of the surface.

The degree of corrosion protection offered by organic coatings is often more affected by the metal surface preparation and pretreatment and by primer composition rather than by top coat composition [79]. This is particularly true for coil coatings where the film thickness (typically  $\sim 1$ mil) offers little protection from water vapor and oxygen permeation. Paint pretreatments such as phosphates and chromates are designed not only to improve adhesion but to passivate the steel surface leading to a high degree of underfilm corrosion protection. Further protection is provided by inhibitive pigmentation such as zinc or strontium chromates within the primer system.

In general, there are no widely employed corrosion standards for prepainted steel. The relative performance of various generic coatings is reasonably well known, and the appropriate standards for any particular application are established between paint supplier and the coil coater. Typically, a 10-year warranted coating for exterior building panel applications would be required to meet the corrosion and durability criteria outlined in Table 3.

TABLE 3-Typical	requirements	to	meet	а	10-year	coating	warranty	for	exterior	building
	-		panel	aj	oplication	ns.				

Accelerated Tests	
Salt Spray (ASTM B 117–64)	<ul> <li>A. 1000 hours—No blistering or loss of adhesion on score line when tested with No. 600 Scotch tape.</li> <li>B. 1500 hours—No more than 20% of the area may contain blisters: none larger than ASTM D 714-56 #6. No loss of adhesion further than 1/8 in. from score line when tested with No. 600 Scotch tape.</li> </ul>
Humidity (ASTM D 1735–62)	<ul> <li>A. 500 hours—May show only slight softening and no blistering.</li> <li>B. 1000 hours—Slight softening with no more than 10% ASTM D 714-56, # 8 blisters.</li> </ul>
Water Immersion (77 deg F- Distilled Water)	A. 500 hours—Shall show no marked color change after a 24-h recovery period.
Accelerated Weathering	Atlas XW-R "Dew Cycle" weatherometer—300 light hours (600 total hours). No adhesion loss or spotting (other than normal water spotting) will be acceptable. Slight fading and no chalking as tested with No. 600 Scotch tape.
Weathering	South Florida—45 degrees South. After 5 years the painted surface shall show no evidence of checking, cracking, blistering, or loss of adhesion. There shall be no more than slight chalking (#9 ASTM D 659–65) and slight color fade (5 NBS units).

### **Stainless Steels**

Although constituting only a very small proportion of total steel shipments, the corrosion test procedures involved in establishing utilization feasibility and design limitations for the stainless steels are probably more numerous and extensive than those for all coated and uncoated low-alloy steels combined. The reason for this is basically twofold and results from (1) the increased aggressiveness of those environments to which the stainless steels are exposed and (2) the localized nature of corrosion attack which can lead to catastrophic failure. These localized forms of corrosion behavior, although found on non-passive low-alloy steels, tend to be more pronounced for the passive stainless steels and include intergranular corrosion, pitting corrosion, crevice corrosion and stress-corrosion cracking. Furthermore, susceptibility to hydrogen cracking becomes greater with the increase in tensile strength associated with many of the heat treated higher alloy steels. The increased susceptibility of the stainless steels to these localized forms of corrosion attack derives in simplest terms from the nature of the small anode-large cathode galvanic cell produced on breakdown or rupture of the passive film often enhanced by local compositional differences. Although the presence or absence of a passive film is a function of environment composition [80], the stainless steels are characterized by the presence of a passive film over a broad range of environment pH, temperature and ionic species. Stainless steels are normally recognized as iron-base alloys containing a minimum of 12 percent chromium, although this level has been shown to be modified slightly due to the addition of other alloying elements. At the 12 percent chromium level, the critical current for passivity in neutral and slightly acid solutions is sufficiently small as to permit spontaneous passivity is induced in aerated solutions is a function of alloy composition and values for the common stainless steels are shown in Table 4 [81].

Many factors can contribute to local attack on metal surfaces and are covered in the excellent review paper by Payer and Staehle [82]. These authors discuss localized corrosion processes in terms of homogeneous (dissolution at solute segregates, grain boundaries) and heterogeneous (second phases) phenomena.

Improper heat treatment of both ferritic and austenitic stainless steels may cause compositional changes at grain boundary areas resulting from either solute segregation or precipitation. A schematic representation of these conditions is shown in Fig. 5, taken from the work of Aust, Armijo and Westbrook [83]. A general review of solute redistribution at grain boundaries has been published by Westbrook [84]. The heat treatment necessary to produce solute distribution at grain boundaries sufficient to cause accelerated attack is known as sensitization, and the time-temperature requirements necessary to induce such a condition differ considerably for the ferritic and austenitic stainless steels. The sensitizing temperature range for austenitic steels is in the range 750 to 1550 deg F, such that slow cooling or prolonged heating operations in this temperature range produce susceptibility to intergranular attack. Sensitization of asutenitic steels results in diffusion of carbon to the grain boundaries and precipitation of chromium carbides, resulting in a chromium depleted zone at some finite distance from the boundary. It has been clearly established that degree of susceptibility to this form of failure is strongly influenced by carbon content to the extent that austenitic stainless steels containing carbon in the range below 0.02 percent are relatively immune to this form of attack [85]. At temperatures higher than the sensitizing range, the mobility of carbon is sufficiently great to cause a uniform distribution throughout the alloy, while at lower temperatures the diffusion rate is not sufficient to cause major migration to grain boundaries (within reasonable time limits).



FIG. 5—Schematic representation of grain boundary segregation effects.

In addition to minimizing intergranular corrosion by reduction in carbon level, significant reductions in susceptibility may be achieved by stabilizing the carbon with titanium or columbium. In certain cases, heat treatment at temperatures in the range 1900 to 2000 deg F followed by quenching may be used to dissolve chromium carbides, and in this manner cause desensitization of a susceptible alloy. Other metallurgical effects (for example grain growth) may preclude such heat treatments, however.

The most commonly used corrosion test for determining intergranular corrosion susceptibility due to compositional variations in grain-boundary areas is a modification of that first described by Huey [86] in 1930 and involves exposure to a boiling solution of 65 percent nitric acid. Data is normally reported in inches penetration/month for each of five 48-h successive tests. A nonspecific ASTM standard method for total immersion corrosion testing of stainless steels is designated A 279–63, while ASTM A 262–70 describes procedures for detecting susceptibility to intergranular attack in stainless steels. Within the scope of the latter designation is included oxalic acid, ferric sulfate-sulfuric acid, nitric acid, nitric-hydrofluoric acid (for molybdenum-bearing austenitic steels) and copper-copper sulfate sulfuric acid environments. Intergranular corrosion due to chromium carbide precipitation is detected by all five test environments, whereas high

corrosion rates due to sigma phase precipitation in wrought chromiumnickel-molybdenum and titanium or columbium stabilized steels are observed only in nitric acid plus ferric sulfate-sulfuric solutions, respectively. A less sensitive test for detecting intergranular corrosion than that described in A 262 is contained in ASTM A 393–63, this being an acidified copper sulfate test for use on severely sensitized alloys. This latter test is based on that initially described by Strauss et al [87].

Nonsensitized (including stabilized) grades of austenitic stainless steel have been found to show intergranular corrosion in highly oxidizing media which has been attributed to grain boundary segregation of phosphorus and silicon [88,89]. Intergranular corrosion of ferritic stainless steels has also been reported [90,91], although the conditions under which sensitivity occurs and the degree of susceptibility are quite different from those for the austenitic grades [92].

The localized corrosion of stainless steels by pitting in chloride-containing solutions including sea water has been recognized for many years [93]. It has been established that pitting also occurs in bromide solutions. Susceptibility is reduced with molybdenum additions, and in this respect AISI Type 316 stainless steel is less susceptible than Type 304. Nickel additions also reduce susceptibility, although less significantly than molybdenum and the austenitic grades are, therefore, generally less susceptible than the martensitic or ferritic stainless steels. Pitting is readily induced in chloride solutions containing oxidizing cations which cause depolarization of the cathodic reduction process. In this respect, ferric chloride has been used for many years to evaluate the resistance of stainless steels to localized pitting attack and a description of the test procedure was first described by Smith [94]. It should be noted, however, that the test tends to be erratic (probably greatly influenced by surface imperfections) and thus is used only to qualitatively determine gross differences in pitting susceptibility between materials.

Brennert [95] established the existence of a "breakthrough" potential at which pitting initiates, which was investigated in some greater detail by Mahla and Nielson [96]. More recent studies [97–101] have attested to the validity of the "critical potential" ( $V_c$ ) as a parameter in quantitatively comparing the susceptibility of stainless steels to the initiation of pitting corrosion. Thus, for passive Type 304 (18 Cr–8 Ni) stainless steel, the corrosion potential must be more noble than 0.26V (versus standard hydrogen electrode) in 0.1 N NaCl at 25 deg C in order to induce pitting [102]. The effect of chloride ion concentration and pH on the critical pitting potential for Type 304 stainless steel is shown in Fig. 6 [100]. In addition to providing a rapid method for evaluating the tendency for localized pitting attack, measurements of critical pitting potentials in conjunction with statistical regression analysis of alloying element effects show promise as a tool in the development of pit resistant stainless steels.

Although the factors contributing to intergranular corrosion failure are



FIG. 6—Critical pitting potential ( $V_{o}$ ) versus pH and chloride ion concentration for AISI type 304 stainless steel.

now reasonably well understood, considerable controversy continues to exist in the area of transgranular stress-induced cracking of stainless alloys in certain specific environments. Tensile stresses are a prime requirement for this mode of failure and time-to-failure is a function of applied stress. In general, there is no clear-cut threshold stress below which failure does not occur for even extended testing times.

Ferritic nickel-free stainless steels are essentially immune to stress corrosion cracking both in the chloride and hydroxyl media which cause rapid failure in stressed austenitic materials. On the other hand, austenitic stainless steels containing greater than 45 percent nickel are again immune to stress-corrosion cracking [103] in chloride solutions. Transgranular stresscorrosion cracking of austenitic stainless steels generally requires high temperature and the most commonly utilized test media for determination of cracking susceptibility is a boiling (154 deg C) solution of 42 percent magnesium chloride. ASTM Subcommittee G01.06 has established a recommended practice for the boiling magnesium chloride test which was first described by Schiel [104] in a study of the cracking susceptibility of various stainless steels. A detailed review of available information on the

	Critic	cal pH
AISI Type	Sulfate	Chloride
304	1.4	1.4
430	4.0	2.3
410	5.0	2.6

TABLE 4—Critical pH values for spontaneous development of passivity for stainless steels in sulfate and chloride solutions,

stress-corrosion cracking of iron-nickel-chromium alloys has been published by Latanision and Staehle [105]. A similar review of the stresscorrosion cracking behavior of high-strength steels is provided in the same publication by Phelps [106].

It should be noted that at the present time there is a lack of standardized stress-corrosion test methods for both stainless and high-strength alloy steels in general. Continued activity by ASTM Subcommittee G01.06 is directed towards the development of recommended practices in the standardization of test specimen configuration, method of stressing, precracking and laboratory test environments.

#### Conclusion

The scope of the present subject has precluded more than a superficial survey of corrosion control and standard test procedures for ferrous-base products. At some time in the future it may be appropriate to subdivide the subject matter into separate areas of review, and in this manner effect a more in-depth evaluation into corrosion testing and quality control test procedures for the various ferrous-base product categories.

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## APPENDIX A-1

Tablulated List of Current Corrosion Standards, Test Methods, and Recommended Practices Issued by the American Society for Testing and Materials (ASTM) and the National Association of Corrosion Engineers (NACE)

American Society For Testing and Materials, 1916 Race Street, Philadelphia, Pa., 19103.

Designation	Title
A 262–68(3) ¹	Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels
A 279-63(3)	Total Immersion Corrosion Test of Stainless Steels
A 296–68(2)	Specification for Corrosion Resistant Iron-Chromium, Iron-Chromium-Nickel, and Nickel Base Alloy Castings for General Application
A 380-57(3)	Recommended Practice for Descaling And Cleaning Stain- less Steel Surfaces
<b>A</b> 393–63(3)	Recommended Practice for Conducting Acidified Copper Sulfate Test for Intergranular Attack in Austenitic Stainless Steel
<b>B</b> 117-64(7, 21, 31)	Salt Spray (Fog) Testing
<b>B</b> 287–62(7, 21, 31)	Acetic Acid-Salt Spray (Fog) Testing
<b>B</b> 368–68(7, 21)	Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)
<b>B</b> 380–65(7)	Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure
B 537-70(7)	Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure
<b>B</b> 538–70(7)	Method of FACT (Ford Anodized Aluminum Corrosion Test) Testing
C 464-64(14)	Test for Corrosion Effect of Thermal Insulating Cements on Base Metal
C 621–68(13)	Test for Static Corrosion of Refractories by Molten Glass
C 622–68(13)	Simulated Service Test for Corrosion Resistance of Re- fractories to Molten Glass
D 69-67(28)	Specification for Friction Tape for General Use for Elec- trical Purposes
D 130-68(17)	Test for Detection of Copper from Petroleum Products, by the Copper Strip Tarnish Test
D 484–71(17)	Specification for Hydrocarbon Drycleaning Solvents
D 665–60(17)	Test for Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water
D 801-57(20)	Dipentene, Sampling and Testing
D 807-52(23)	Corrosivity Test of Industrial Water (United States Bureau of Mines Embrittlement Detector Method)

¹ Numbers in parentheses indicate the part number of the Book of Standards in which the standard appears, as of 15 July 1971. Standards are also available separately. The number after the dash is the year of adoption or of latest revision.

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Designation	Title
D 849-47(20)	Test for Copper Corrosion of Industrial Aromatic Hydro- carbons
D 930-67(22)	Total Immersion Corrosion Test of Water-Soluble Alumi- num Cleaners
D 11/1-52(23)	Specification for Substitute Ocean Water
D 1261 - 55(17)	Test for Effect of Grease on Conner
$D_{1201} = 33(17)$ $D_{1275} = 67(18, 20)$	Test for Corresive Sulfur in Electrical Insulating Oils
D 1275-67(18, 29) D 1280-67(22)	Total Immersion Corrosion Test for Soak Tank Metal
	Cleaners
D 1374–57(22)	Aerated Total Immersion Corrosion Test for Metal Cleaners
D 1384–70(22)	Corrosion Test for Engine Antifreezes in Glassware
D 1567-62(22)	Testing Detergent Cleaners for Evaluation of Corrosive Effects on Certain Porcelain Enamels
D 1611-60(15)	Test for Corrosion Produced by Leather in Contact with
	Metal
D 1616-60(20)	Test for Copper Corrosion by Mineral Spirits (Copper Strip Test)
D 1654-61(21)	Evaluation of Painted or Coated Specimens Subjected to
/	Corrosive Environments
D 1735-62(21)	Water Fog Testing of Organic Coatings
D 1743-64(17)	Test for Rust Preventive Properties of Lubricating Greases
D 1838-64(18, 19)	Test for Copper Strip Corrosion by Liquified Petroleum
	(LP) Gases
D 2043-69(15)	Test for Silver Tarnishing by Paper
D 2059–63(25)	Test for Resistance of Zippers to Salt Fog
D 2251–67(22)	Test for Metal Corrosion by Halogenated Organic Solvents
	and Their Admixtures
D 2570–70(22)	Simulated Service Corrosion Testing of Engine Antifreezes
D 2649–70(18)	Determining Corrosion Characteristics of Dry Solid Film Lubricants
D 2688-70(23)	Test for Corrosivity of Water in the Absence of Heat Transfer (Weight Loss Methods)
D 2776-69T(23)	Tests for Corrosivity of Water in the Absence of Heat
D 2002 70(21)	Transfer (Electrical Methods), Tentative
D 2803-70(21)	Test for Finform Corrosion Resistance of Organic Coatings
T 2000 (0T(22)	On Metal
D 2809-091(22)	Aluminum Automotive Water Pumps with Coolants,
(2, 1, 72(21))	lentative
G = 1 - 12(31)	Evaluating Corrosion Test Specimens
G 2–67(7, 31)	Recommended Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys
G 3-68(31)	Recommended Practice for Conventions Applicable to
0 5 00(51)	Electrochemical Measurements in Corrosion Testing
G 4-68(3, 31)	Recommended Practice for Conducting Plant Corrosion
0 + 00(5, 51)	Tests
G 5-72(31)	Recommended Practice for a Standard Reference Method
	for Making Potentiostatic and Potentiodynamic Anodic
	Polarization Measurements
G 7-69T(30)	Recommended Practice for Atmospheric Exposure Testing
	of Nonmetallic Materials, Tentative

Designation	Title
G 9-69T(21, 30)	Test for Water Penetration into Pineline Coatings. Tentative
G 11-69T(21, 30)	Test for Effects of Outdoor Weathering on Pipeline Coatings, Tentative
G 15-71(31)	Definitions of Terms Relating to Corrosion and Corrosion Testing
G 16–71(31)	Recommended Practice for Applying Statistics to Analysis of Corrosion Data
G 28–72	Method of Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich Chromium Bearing Alloys
G 30-72	Recommended Practice for Making and Using U-Bend Stress Corrosion Test Specimens
G 31–72	Recommended Practice for Laboratory Immersion Cor- rosion Testing of Metals
G 33-72	Recommended for Recording Data from Atmospheric Corrosion Tests of Metallic Coated Steel Specimens
G 34-72	Standard Method of Test for Exfoliation Corrosion Sus- ceptibility in 7XXX series Copper-Containing Aluminum Alloys (Exco Test)
G 35-73	Recommended Practice for Determining the Susceptibility of Stainless Steel and Related Ni-Cr-Fe Alloys to Stress Corrosion Cracking in Polythionic Acids
G 36–73	Recommended Practice for Performing Stress Corrosion Cracking Tests in a Boiling Magnesium Chloride Solution
G 37–73	Recommended Practice for the Use of Mattsson's Solution of pH 7.2 to Evaluate the Stress Corrosion Susceptibility of Cu-Zn Alloys

National Association of Corrosion Engineers, 2400 West Loop South, Houston, Texas, 77027.

TM-01-69 ²	Laboratory Corrosion Testing of Metals for the Process Industries
RP-01-69	Control of External Corrosion on Underground or Sub- merged Pining Systems
TM-01-70	Visual Standard for Surfaces of New Steel Airblast Cleaned with Sand Abrasive
<b>RP</b> -01-70	Protection of Austenitic Stainless Steel in Refineries Against Stress Corrosion Cracking by the Use of Neutralizing Solu- tions During Shut Down
TM-02-70	Method of Conducting Controlled Velocity Laboratory Corrosion Tests
TM-01-71	Autoclave Corrosion Testing of Metals in High-Tempera- ture Water
<b>RP01-71</b>	Method for Lining of Lease Production Tanks with Coal Tar Enoxy
TM-01-72	Antirust Pronerties of Petroleum Products Pineline Cargoes
RP01-72	Surface Preparation of Steel and Other Hard Materials by Water Blasting Prior to Coating or Becoating
RP0272	Direct Calculation of Economic Appraisals of Economic Control Measures

 $^{\rm 2}$  The last two digits indicate the year of adoption. TM denotes a test method and RP a recommended practice.

Designation	Title
RP-03-72	Methods for Lining Lease Production Tanks with Coal Tar Epoxy
RP-04-72	Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments
RP05-72	Design, Installation, Operation, and Maintenance of Im- pressed Current Deep Ground Beds
TM-01-73	Methods for Determining Water Quality for Subsurface Injection Using Membrane Fitters
RP0173 RP0273	Collection and Identification of Corrosion Products Handling and Proper Usage of Inhibited Oil Field Acids

# APPENDIX A-2

### Selected Tabulation of British, French, and German Standards Concerned with Corrosion Testing Methods and the Evaluation of the Corrosion Resistance of Materials and Products

British Standards: Issuing Agency-British Standards Institution Designation Title and Description B.S. 135 Specifications for Benzines and Benzoles The corrosive sulfur content is specified in terms of the discoloration of a freshly prepared copper strip exposed in a reflux condenser. B.S. 245 Specifications for White Spirit Similar to B.S. 135 **B.S.** 441 Rosin-Cored Solder Wire "Activated" and "Non-Activated" (Non-corrosive) The corrosive action of flux residue is assessed in terms of the discoloration and possible pitting of a copper sheet exposed to the flux at 35 C for 48 h. **B.S.** 489 Specification for Steam Turbine Oils Specifies corrosivity, rust preventing characteristics, and oxidation behavior in terms of ASTM Standard Methods D 130, D 665, D 943, and D 974. B.S. 1133 British Standard Packaging Code. Section 6. Temporary Prevention of Corrosion Salt, humidity, and hydrogen bromide exposure tests are used to evaluate the effectiveness of corrosion inhibiting coatings and solutions. B.S. 1224 Specification for Electroplated Coatings of Nickel and Chromium CASS, Corrodkote, and acetic acid salt spray tests (similar to ASTM B 368, B 380, and B 287) are used to evaluate corrosion resistance. B.S. 1263 Hypodermic Syringes for Use in Medical and Surgical Practice Autoclaving in steam, boiling in distilled water, and boiling in 0.9 percent sodium chloride solution consecutively for 30 min each, are used to evaluate corrosion resistance. B.S. 1344 Part 2A Vitreous Enamels-Group A, Kitchen Equipment Disks of filter paper saturated with 100 g/l of citric acid are placed onto the surface and the deterioration observed after 20 min at 20 C. B.S. 1391 Performance Tests for Protection of Light-Gauge Steel and Wrought Iron Against Corrosion Corrosion tests are described involving either daily exposure to a sea water spray or continuous exposure to vapor condensation above a heated solution of sulfur dioxide. These tests are aimed at evaluating both metallic and paint coatings. B.S. 1615 Anodic Oxidation Coatings for Aluminum An acetic salt spray test (similar to ASTM B 287) and the sulfur dioxide test of B.S. 1391 are used to evaluate corrosion resistance and effectiveness of scaling. B.S. 1706 Specification for Electroplated Coatings of Cadmium and Zinc on Iron and Steel

Designation	Title and Description
The effectiveness of p humidity exposure at 5	passivation is measured by means of a 95-percent relative $55 \text{ C}$ for 16 h, followed by cooling to 30 C and holding for 1 h.
B.S. 1872	Specification for Electroplated Coatings of Tin
Exposure to a contro coating discontinuities	lled moist sulfur dioxide atmosphere is used to determine
B.S. 1916	Hypodermic Syringes for Insulin Injection
The same procedure a	s in B.S. 1263 is used to evaluate corrosion resistance.
<b>B.S.</b> 2011	Basic Climatic and Durability Tests for Components for Radio and Allied Electronic Equipment
A 2-h synthetic sea wa	ter spray at 20 C followed by storage at 35 C and 90-95 per-
cent relative humidity	is used. Humidity tests at 55 C and 95 percent humidity with
2 deg C temperature fl	uctuations four times an hour are also included
B.S. 2056	Rust, Acid, and Heat Resisting Steel Wire for Springs
Susceptibility to interg followed by exposure t	ranular corrosion is evaluated by a sensitizing heat treatment to a solution of copper sulfate and sulfuric acid.
B.S. 2983	Hypodermic Dental Needles
A 5-h exposure to 10	percent citric acid solution at room temperature followed by
boiling in distilled wat	er for 30 min is used.
<b>B.S. 3116</b>	Specification for Automatic Fire Alarm Systems in Buildings Part I. Heat-Sensitive (Point) Detectors
A 16-day exposure to	condensing sulfur dioxide is used, similar to that detailed in
B.S. 1391.	
B.S. 3597	Specification for Electroplated Coatings of 65/35 Tin- Nickel Alloy
A 24-h exposure to a	controlled sulfur dioxide atmosphere at room temperature is
used to evaluate the p	resence of discontinuities.
B.S. 3745	Method for the Evaluation of Results of Accelerated Corrosion Tests on Metallic Coatings
A detailed procedure	for the counting and evaluation of corrosion sites observed
after acetic acid salt s	pray, Corrodkote, and CASS tests is described.
<b>B</b> .S. 4601	Specification for Electroplated Coatings of Nickel Plus Chromium on Plastic Materials
CASS and acetic acid	salt spray tests are used.
<b>B</b> .S. 4292	Specification for Electroplated Coatings of Gold and Gold Alloy
Exposure to sulfur di	oxide followed by exposure to hydrogen sulfide is used for
coatings greater than thinner coatings.	5 $\mu$ m thick while hydrogen sulfide exposure alone is used for
<b>B</b> .S. 4758	Specification for Electroplated Coatings of Nickel for Engineering Purposes
Exposure to sodium c by dipping into a sol porosity.	hloride and gelatine-soaked filter papers for 10 min followed ution of potassium ferricyanide is used to evaluate coating
French Standards: Is (AFNOR)	suing Agency-L'Association Francaise De Normalisation

NF X 41-002 Essai au brouillard salin

Gives specifications for both 5 and 20 percent salt spray testing at 35 C and 85–90 percent relative humidity.

Designation		Title ar	nd Description			
NF A 91-020	Revêtements	Métalliques	Clichés-Étalons	Pour	Essais	de

Corrosion

Provides color photographs showing the difference in behavior of an anodic metal plating (zinc) and a cathodic metal plating (nickel) on steel during salt spray testing.

NF A 05–159 Détermination de la Résistance a la Corrosion Intergranulaire des Aciers Inoxydables Austénitiques

Describes the determination of intergranular corrosion susceptibility in austenitic stainless steels using the Monypenny-Strauss Test (immersion in a solution of sulfuric acid and copper sulfate).

NF A 91-021 Méthode d'Évaluation des Résultats des Essais de Corrosion, Applicable aux Dépots Électrolytiques Cathodiques

Provides a detailed rating procedure and classification system for evaluating (in conjunction with NF A 91–020) the performance of cathodic metal electroplates in accelerated corrosion tests.

NF A 05–160 Détermination de la Resistance à la Corrosion Intergranulaire des Aciers Inoxydables Austenitiques Essai de Corrosion en Milieu Nitrique

Describes the determination of intergranular Corrosion susceptibility in austenitic stainless steels by means of the Huey Test (nitric acid exposure).

German Standards: Issuing Agency—Fachnormenausschuss Materialprüfung im Deutschen Normenausschuss

Designation	Title
DIN 1548	Zinküberzüge runder Stahldrähte
DIN 2444	Entwurf, Zinküberzüge auf Stahlrohren: Technische Liefer-
	bedingungen für Feuerverzinkung in handelsüblicher Qualität
DIN 8565	Rostschutz von Stahlbauwerken durch Metallspritzen
<b>DIN 20578</b>	Zinküberzüge für Förderwagen; Feuerverzinkung der
	Kästen
<b>DIN 50010</b>	Werkstoff-, Bauelemente- und Geräteprüfung; Klima-
	beanspruchung, Allgemeines, Begriffe
DIN 50016	Werkstoff-, Bauelemente- und Geräteprüfung; Bean-
	spruchung im Feucht-Wechselklima
DIN 50017	Werkstoff-, Bauelemente- und Geräteprüfung; Bean-
	spruchung in Schwitzwasser-Klimaten
DIN 50018	Werkstoff-, Bauelemente- und Geräteprüfung; Bean-
	spruchung im Schwitzwasser-Wechsel-klima mit schwefel-
	dioxydhaltiger Atmosphäre
DIN 50021	Vornorm Korrosionsprüfungen; Sprühnebelprüfungen mit
	verschiedenen Natriumchloridlösungen
DIN 50900	Korrosion der Metalle; Begriffe
DIN 50901	Korrosionsgroben bei ebenmässigem Angriff; Begriffe,
	Formelzeichen, Einheiten
DIN 50902	Entwurf Korrosionsschutz; Behandlung von Metallober-
	flächen, Begriffe
DIN 50903	Metallische Überzüge; Poren, Einschlüsse, Blasen und
	Risse, Begriffe
DIN 50905	Korrosionsversuche; Richtlinien für die Durchführung und
	Auswertung

Designation	Title
DIN 50906	Korrosionsprüfung in kochenden Füssigkeiten
	(Kochversuch)
DIN 50907	auf Meerklima- u. Meerwasserbestädigkeit, für Leicht- metalle
DIN 50908	Prüfung von Leichtmetallen; Spannungskorrosionsversuche
DIN 50910	Einflussgrössen und Messverfahren bei der Korrosion im
	Erdboden in Gegenwart von elekrischen Erdströmen
DIN 50911	Prüfung von Kupferlegierungen; Quecksilbernitratversuch
DIN 50914	Prüfung nichtrostender Stähle auf Beständigkeit gegen interkristaline Korrosion; Kupfersulfat-Schwefelsäure- Verfahren
DIN 50930	Vornorm Korrosion der Metalle; Beurteilung des korrosion- schemischen Verhaltens kalter Wässer gegenüber unver- zinkten und vorzinkten Fiscenwerkstoffen Biehtlinien
DIN 50932	Prüfung metallischer Überzüge; Bestimmung der Dicke von Zinküberzügen auf Stahl durch örtliches anodisches Ablösen
DIN 50933	Entwurf, Prüfung metallischer Überzüge; Messung der Dicke von Überzügen auf Stahl mittels Feinzeigers
DIN 50938	Entwurf, Korrosionsschutz; Brünieren von Eisenwerk- stoffen
DIN 50940	Prüfung von chemischen Entrostungsmitteln und Spar- beizzusätzen (Inhibitoren) für Stahl und Eisen: Labora- toriumsversuche
DIN 50941	Korrosionsschutz; Chromatieren von galvanischen Zink- und Cadmiumüberzügen
DIN 50942	Entwurf, Korrosionsschutz: Phosphatieren von Stahlteilen
DIN 50943	Prüfung von anorganischen nichtmetallischen Überzügen auf Aluminum und Aluminiumlegierungen; mikroskopishe Messung der Schichtdicke
DIN 50944	Prüfung von anorganischen nichtmetallischen Überzügen auf Reinaluminum und Aluminumlegierungen; Bestimmung des Flächengewichtes von Aluminiumoxidschienten durch chemisches Ablösen
DIN 50945	-; Zerstörungstreie Messung der Dicke transparenter Oxidschichten nach dem Differenzverfahren mit dem Mikro- skop
DIN 50946	-; Prüfung der Güte der Verdichtung anodisch erzeugter Oxidschichten im Anfärbeversuch
DIN 50947	-; Prüfung anodisch erzeugter Oxidschichten im Korro- sionsversuch (Dauertauchversuch)
DIN 50948	Prüfung von anorganischen nichtmetallischen Deckschichten auf Reinaluminum und Aluminiumlegierungen; zerstörungs- freie Messung der Schichtdicke von transparenten Oxid- schichten nach dem Lichtschnittwerfahren
DIN 50949	Prüfung von anorganischen nichtmetallischen Überzügen auf Reinaluminum and Aluminumlegierungen; Zerstörungs- freie Prüfung von anodisch erzeügten Oxidschichten durch Messung des Scheinleitwertes
DIN 50950	Prüfung galvanischer Überzüge; mikroskopische Messung der Schichtdicke
DIN 50951	Entwurf, Prüfung galvanischer Überzüge; Messung der Dicke galvanischer Überzüge nach dem Strahlverfahren

Designation	Title
DIN 50952	Prüfung metallischer Überzüge; Bestimmung des Flächen- gewichtes von Zinküberzügen auf Stahl durch chemisches- Ablösen des Überzüges gravimetrisches Verfahren
DIN 50953	Prüfung galvanischer Überzüge; Bestimmung der Dicke von dünnen Chromüberzügen nach dem Tünfelverfahren
DIN 50954	Prüfung metallischer Überzüge; Bestimmg. des mittleren Flächengewichtes von Zinnüberzügen auf Stahl durch chem. Ablösen des Überzüges
DIN 50955	Entwurf, Prüfung metallischer Überzüge; Messung der Dicke galvanischer Überzüge, coulometrisches Verfahren
DIN 50957	Prüfung galvanisher Bäder; Galvanisierungsprüfung mit der Hull-Zelle, allgemeine Grundsätze
DIN 50958	Entwurf, Prüfung galvanischer Überzüge; Korrosions- prüfung von verchromten Gegenständen nach dem modifi- zierten Corrodkote-Verfahren
DIN 50960	Korrosionsschutz; galvanische Überzüge, Kurzzeichen, Schichtdicken, allgemeine Richtlinien Bbl. Vornorm, Galvanische Überzüge auf Stahl; allgemeine Hinweise zur Anwendung als Schutz gegen atmosphärische Korrosion in Mittel- und Westeuropa
DIN 50961	Korrosionsschutz: galvanische Zinküberzüge auf Stahl
DIN 50962	Korrosionsschutz; galvanische Kadminiumüberzüge auf Stahl
DIN 50963	Korrosionsschutz; galvanische Nickel- und Nickel-Chrom- Überzüge auf Stahl
DIN 50964	Korrosionsschutz; galvanische Kupfer-Nickel-Chrom- Überzüge auf Zink und Zinklegierungen
DIN 50965	Korrosionsschutz; galvanische Zinn- und Kupfer-Zinn- Überzüge auf Stahl, Kupfer und Kupferlegierungen
DIN 50967	Entwurf, Galvanische Überzüge, Nickel-Chrom-Überzüge auf Stahl, Kupfer und Zinkwerkstoffen sowie Kupfer- Nickel-Chrom-Überzüge auf Stahl und Zinkwerkstoffen
DIN 50971	Entwurf, Bl.1, Elektrolytisch erzeugte Überzüge; Chemi- kalien für cyanidische Bäder, Anforderungen
DIN 50972	Entwurf, Bl.1, Elektrolytisch erzeugte Überzüge; Kupfer- sulfat für galvanische Bäder, Anforderungen
DIN 50973	Entwurf, Bl.1, Elektrolytisch erzeugte Überzüge; Säuren für galvanische Bäder. Anforderungen
DIN 50975	Korrosionsschutz; Zinküberzüge durch Feuerverzinken, Richtlinien
DIN 50976	Entwurf, Anforderungen an Zinküberzüge auf Gegenstanden aus Eisenwerkstoffen, die als Fertigteile feuerverzinkt werden
DIN 50980	Entwurf, Prüfung metallischer Überzüge; Auswertung von Korrosionsprüfungen
DIN 51213	Vornorm Prüfung metallischer Überzüge auf Drähten

## **APPENDIX B**

Selected ASTM Standards Referred to Frequently in Book

Designation: A 279 - 63

American National Standard G81 9-1970 American National Standards Institute

## Standard Method of TOTAL IMMERSION CORROSION TEST OF STAINLESS STEELS¹

This Standard is issued under the fixed designation A 279: the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reproval.

#### 1. Scope

1.1 This method describes procedures for making total immersion corrosion tests on stainless steels. No one procedure is rigorously described since the most desirable procedure to follow in any specific case will depend on the particular aim desired.

1.2 When the total immersion test is to serve as a control test for determining whether successive lots of the same material differ significantly in some property from each other, the test conditions should be arbitrarily selected and closely controlled so that any variation in results can safely be attributed to variations in the material being tested.

1.3 When the test is used to assist in the choice of material for a specific use, the test conditions should simulate the conditions of service as closely as practical. Where the temperature and composition of the solution, aeration, and similar factors vary widely under service conditions, rigorous control of these factors is not necessary, provided all of the competing materials are subjected to the same exposure conditions.

1.4 In designing any total immersion test, consideration should be given to the various factors discussed in this method since these factors have been found to be of importance in affecting the results obtained.

#### 2. Apparatus

2.1 Any apparatus capable of providing the proper control of the important factors: aeration, temperature, and velocity, may be used to achieve the required degree of reproducibility in a total immersion corrosion test. Methods for control of temperature and aeration will be essentially the same with all types of apparatus. The principal differences will be with respect to the means of providing a control of the velocity.

2.2 Velocity:

2.2.1 Ordinarily, velocity will be fixed at some value which shall be held uniform over the whole surface of the specimen, especially when changes in mechanical properties are to be used as a measure of corrosion; however, for particular purposes it may be desired to vary the velocity from point to point on a specimen. Any device for moving a specimen through a solution, or a solution past a specimen, as through a tube, will be satisfactory provided that relative motion can be held constant and when desired, substantially uniform over the whole surface of the specimen (Note 1). It should be recognized that at very high rates of motion the effects of skin friction will reduce the true velocity below the apparent velocity without, however, interfering with the reproducibility of tests made with the same apparatus.

NOTE 1: Example—Specimens may be moved in a vertical, circulating path,² or specimens may be

¹This method is under the jurisdiction of ASTM Committee A-1 on Steel, Stainless Steel and Related Alloys, and is the direct responsibility of Subcommittee A01.14 on Methods of Corrosion Testing.

Methods of Corrosion Testing. Current edition accepted Sept. 30, 1963. Originally issued 1944. Replaces A 279 – 44 T.

² For a description of an apparatus to move specimens in a vertical, circular path see Fraser, O. B. J., Ackerman, D. D., and Sands, J. W., "Controllable Variables in the Quantitative Study of the Submerged Corrosion of Metals," *Industrial and Engineering Chemistry*, Vol 19, 1927, pp. 332-338: also Searle, H. E., and LaQue, F. L., "Corrosion Testing Methods," *Proceedings*, Am. Soc. Testing Mats., Vol 35, Part II, 1935, p. 249.

mounted on a carrier attached to a rotating spindle or mounted on the spindle itself in a way that will ensure substantially uniform velocity over the principal surfaces of the specimens when this is desired.⁸ It is also possible to mount a specimen on a rotating disk or spindle, so that the surfaces of the specimens move through the solution at velocities that vary with the distance from the center of rotation. Obviously, this procedure will not measure the effect of a single velocity but rather the combined effect of variable velocities. So long as the other test conditions are kept the same, such variable velocity tests may also be expected to give reproducible results.

2.2.2 The test velocity should approximate that expected in the proposed service use of the alloys or metals being tested. It may be impossible to control the motion of boiling liquids, especially when a reflux condenser is used to prevent rapid loss of some constituent of the testing solution. However, the velocity induced by boiling and aeration together may be sufficient to give satisfactory check results, even though it will not suffice to duplicate service conditions involving high velocity as well as high temperature.

2.2.3 Where velocity appears to be the controlling factor, tests should be made at different velocities, keeping the other conditions constant. In some cases it may be proper to omit any kind of mechanical stirring; however, it should be recognized that zero velocity is difficult to maintain and that stagnant tests shall be subjected to exceptionally careful control to achieve a proper degree of reproducibility.

2.3 Temperature Control—The temperature of the corroding solution should be controlled within  $\pm 2$  F (1 C). For control testing at room temperature, it is suggested that the solution be maintained at 95  $\pm 2$  F (35  $\pm 1$  C) which, being slightly above most room temperatures, is easy to maintain by heat input. When a water bath is used to maintain the proper temperature, the level of the water in the bath should be the same or slightly above the level of the solution in the test jars. The water bath should be large enough to permit free circulation of the water around the test jars.

2.4 Aeration:

2.4.1 The degree of aeration should be subjected to close control. It is not possible to do this by depending on diffusion from the surface of the solution to maintain uniform conditions even in a well-agitated solution. To achieve air saturation, the solution should be aerated by

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blowing air through it using an Alundum thimble⁴ or a sintered glass diffusion disk of medium porosity to break the air stream up into small bubbles. Such air bubbles should be introduced at the base of a glass chimney over each aerator so as to prevent the impingement of the stream of air bubbles on the test specimen.

2.4.2 The rate of air flow required to maintain air saturation will depend on the volume of the testing solution, the area of the test specimen, and its rate of corrosion. The volume of air should be measured and controlled as accurately as possible, preferably within  $\pm 10\%$ , by the use of a flowmeter such as a calibrated differential manometer, a rotameter, or other suitable device. The volume of air per litre of testing solution should be at least 20 cm³/min when the recommended solution volume to specimen area (4 litres/dm²) is maintained. If the indicated rate of corrosion should exceed 300 mg/dm²·day, it may be necessary to increase the rate of air flow or to employ some extraordinary means of supplying the oxygen required to maintain saturation. The air should be purified by passing it through some porous packing material, such as wool or excelsior, to remove suspended solids, and then through a solution of sodium hydroxide (approximately 3%) to remove carbon dioxide and sulfur compounds, and finally through a water wash bottle which also serves to humidify the air and avoid crystallization of salts in the pores of the aerator.

2.4.3 When it is desired to maintain the dissolved oxygen concentration at a value lower than the point of saturation with air, this should be accomplished by altering the composition of the saturating gas (as by the addition of nitrogen), rather than by altering the rate of flow of the gas. Similarly, where it is desired to have zero aeration, the solution should be kept saturated with, and under, an atmosphere of an inert gas. such as oxygen-free nitrogen. Merely eliminating aeration will not ensure an air-free solution, nor can reproducible results be expected from such attempts to achieve un-

³ For a description of methods for attaching specimens to a rotating spindle, see *Journal*, Am. Soc. Naval Eng., Vol 55, No. 1, February 1943, pp 64-65.

⁴Thimble RA-98 of the Norton Co., or equivalent, is satisfactory.
aerated solutions. As a general rule, corrosion of stainless steels is retarded rather than accelerated by aeration. Conditions favoring oxygen exclusion, therefore, favor corrosion and represent just as adverse testing conditions for stainless steels as fully aerated solutions do for non-ferrous metals, and ordinary irons and steels.

2.5 Specimen Supports-Supports for the specimens will vary with the apparatus used. but should be designed so as to insulate specimens from each other, and from any metallic container or supporting device used with the apparatus. The supporting device and container should not be affected by the corroding agent to an extent that might cause contamination of the testing solution so as to change its corrosiveness. The shape and form of the specimen support should be such as to avoid, as much as possible, any interference with free contact of the specimen with the corroding solution. Where it is desired to set up conditions favoring contact corrosion, "deposit attack," or other forms of concentrationcell action, the means by which these types of attack are favored should be such as to ensure exact reproducibility from specimen to specimen and test to test.

#### 3. Test Solution

3.1 Test solutions should be made up accurately, using reagents conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society, dissolved in distilled water except in special cases, such as naturally occurring solutions, or those taken directly from some plant process.

3.2 The composition of any test solution should be controlled to the fullest extent possible and, in reporting results, it should be described as completely and as accurately as possible. Chemical content should be reported either as weight percent of the solution, grams per litre, or in terms of normality.

3.3 The composition of the test solution should be checked by analysis at the end of the test to determine the extent of any changes in composition, such as might result from evaporation favored by aeration. Evaporation losses, if any, should be made up by means of a constant level device, or by frequent additions of distilled water, or other components as may

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be required corresponding in composition with the vapors from the solution, so as to maintain the original volume within  $\pm 1\%$ .

3.4 The volume of the test solution should be large enough to avoid any appreciable changes in its corrosiveness either through the exhaustion of corrosive constituents, or the accumulation of corrosion products or other contaminants that might affect further corrosion.

3.5 A recommended ratio between the volume of the test solution and the area of the specimen is  $250 \text{ m1/in.}^2$  of specimen area (4 litres/dm²).

3.6 Whatever volume of test solution is used, possible effects of corrosion on the concentration of corrosive constituents should be determined by analysis, and, when required, appropriate action should be taken by replacing the exhausted constituents or providing a fresh solution.

3.7 When the object of the test is to determine the effect of a metal or alloy on the characteristics of the test solution (for example, the effects of metals on dyes), it is desirable to reproduce the ratio of solution volume to exposed metal area that exists in practice. It is also necessary to take into account the actual time of contact of the metal with the solution. If all of these factors cannot be reproduced directly in the laboratory test. then it will be necessary to make proper allowances as by reducing the time of contact to compensate for necessary decreases in the ratio of volume to area. Any necessary distortion of the testing conditions must be taken into account when interpreting the results.

#### 4. Test Specimens and Their Preparation

4.1 The size and shape of specimen will vary with the purpose of the test, the nature of the materials to be tested, and the testing apparatus to be used. The size may also be limited by the necessity of preserving a proper ratio between the area of the specimen and the volume of the testing solution when the latter must be limited. In general, an effort should be made to have the ratio of surface to mass large and that of edge area to total area small.

4.2 When quantitative determinations of changes in tensile properties are to be used as the principal measure of corrosion, then ten-

sion test specimens or a piece from which such specimens may be cut after exposure shall be used.⁵ In such cases, also, a set of similar specimens should be preserved in a noncorrosive environment for comparison with the exposed corrosion test specimens as to tensile properties.

4.3 The shape and dimensions of specimens shall be such as to permit weighing on an accurate balance and to facilitate accurate measurement and calculation of the area of each specimen. Such measurements of dimensions shall be made to the nearest 0.01 in. (0.25 mm), unless for some special purpose greater accuracy is required.

4.4 All sheared edges should be trimmed beyond the shear marks by sawing, machining, or filing or grinding, with the final cut to be as light as possible so as to minimize hardening and distortion of the edges.

4.5 When the test is being made for engineering purposes and a special finish is specified, it may be desirable to make the surface of the test specimen correspond to the surface to be used in service. In general, however, results that are more reproducible may be expected if a standard surface finish for the test specimens is used.

4.6 It has been shown that more uniform results may be expected if a substantial layer of metal is removed from the specimens to eliminate variations in condition of the original metal surface. This may be done either by a preliminary chemical treatment (pickling) or by surfacing with a coarse abrasive paper or cloth, such as No. 50. The thickness of metal so removed should be at least 0.003 mm or 2 to 3 mg/cm² in the case of heavy metals.

4.7 The final treatment should include resurfacing with No. 120 abrasive paper or cloth or equivalent. This resurfacing may be expected to cause some surface work-hardening to an extent that will be determined by the vigor of the surfacing operation, but is not ordinarily significant. The resurfaced specimens should then be degreased by scrubbing with clean pumice powder, followed if necessary, by rinsing in water and a suitable solvent, such as acetone or a mixture of 50% alcohol and 50% ether. and drying. The use of towels for drying may introduce an error through contamination of the specimens with grease or

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lint. The dried specimens should then be weighed with an accuracy of  $\pm 0.0005$  g.

4.8 Surface passivation sometimes has an important effect on the resistance of stainless steels in certain types of nonoxidizing solutions. It is, therefore, sometimes desirable to use pre-passivated specimens in corrosion tests. This passivation may be accomplished by exposure of the finally polished specimens for 1 h in nitric acid (30 weight, %) at 60 C. Such passivated specimens represent the most nearly identical starting conditions possible for a series of stainless steel specimens (Note 2). If a passivation treatment is employed, it must be recognized that subsequent disturbance of the surface by scraping or abrasion may greatly affect the results obtained under certain conditions of exposure.

NOTE 2—Instead of the passivation treatment just described, it may be desirable simply to clean the surface of the specimens chemically by treatment in nitric acid (10 weight, %) at 60 C for 30 min.

4.9 When the proposed application will require welded assemblages, welded specimens approximating the thickness to be used should be included in the test. Such specimens should represent the same condition of heat treatment and finish as contemplated for the service unit.

4.10 To facilitate interpretation of test results and their duplication by others, the details of the methods of preparation of the specimens should be described when reporting the results of a test.

4.11 The test report should include a description of the nature and composition of the specimens (see Section 9). The composition preferably should be that actually determined by analysis of the material from which the specimens were cut. If it should not be practical to provide this information, then reference should be made to the approximate or nominal composition of the material or, as a last resort, the trade name or grade of the material may be given. The form and metallurgical condition of the specimen, including the nature and sequence of any hot or cold working, welding, and heat-treatment should also be described as completely as possible.

⁶See Figs. 7 and 8 of ASTM Methods E 8, Tension Testing of Metallic Materials, *Annual Book of ASTM Standards*, Part 31.

#### 5. Number of Specimens

5.1 In general, it is recommended that total immersion tests be made in duplicate. For precise work it may be desirable to test a larger number of specimens and for routine tests a single specimen may be considered sufficient. In certain types of nonoxidizing solutions highly variable results may be obtained on stainless alloys with only slight differences in surface or exposure conditions. This should be borne in mind in conducting tests on stainless alloys in, for instance, sulfuric acid solutions.

5.2 Each specimen should preferably be tested in a separate container, since testing several specimens of either the same material or of different materials in a single container may give erratic results. However, under special conditions it may be permissible, or even desirable, to test more than one specimen in a single container provided it is recognized that the corrosion products from a specimen showing a high rate of attack may accelerate corrosion of another specimen, or specimens, in the same container.

#### 6. Methods of Cleaning Specimens After Test

6.1 It is essential that corrosion products be removed from specimens if changes in weight are to be used as a measure of corrosion. There are many satisfactory means of cleaning specimens after exposure, such as the use of bristle brushes with mild abrasives and detergents, treatment with appropriate chemical solutions. especially suitable with certain metals and corrosion products, and electrolytic methods. The use of bristle brushes should ordinarily be limited to heavily corroded specimens. Drastic cleaning methods should not be used when the specimens are small or the amount of weight change expected is slight. For most tests on stainless alloys scrubbing of the specimen with a rubber stopper under running water has been found adequate.

6.2 Whatever the treatment, its effect in removing metal, if any, should be determined for each material and the results of weight loss determinations should be corrected accordingly. The method of cleaning should be reported.

6.3 An electrolytic cleaning method that has been found to be useful with a large number of

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metals and alloys is described in Appendix X1. This method can be used for stainless alloys if desired.

6.4 Other chemical cleaning methods that may be used are:

6.4.1 Treatment in nitric acid (10 weight, %) at 60 C provided no chlorides are present since chlorides will promote attack of the base metal.

6.4.2 Treatment in a hot solution of sodium hydroxide (20%) containing 200 g/litre of zinc dust may be effective in loosening deposits which can then be rubbed off.

6.4.3 Immersion of the specimens in a hot solution of ammonium acetate to remove rust.

#### 7. Duration of Test

7.1 The duration of any test will be determined by its nature and purpose. In some cases it will be desirable to expose a number of specimens so that certain of them can be removed after definite time intervals so as to provide a measure of change of corrosion rates with time. Any procedure that requires removal of solid corrosion products between periods of exposure of the same specimens will not measure accurately normal changes of corrosion with time.

7.2 The higher the rate of corrosion, the shorter may be the testing period.

7.3 Where the object of the test is to predict corrosion rates over a long period, it is obviously desirable to run the test for as long as may be practical, provided that the testing conditions and the corrosive characteristics of the solution can be maintained constant over a long test period.

#### 8. Interpretation of Results

8.1 After the corroded specimens have been cleaned, they should be reweighed with the same accuracy as the original weighing  $(\pm 0.0005 \text{ g})$ . It will then be possible to calculate the loss in weight per unit of area during the test period. This may be used as the principal measure of corrosion.

8.2 Corrosion rates calculated from the loss in weight data should be reported in milligrams per square decimetre per day (24 h), abbreviated mdd. Factors for converting these units to other common corrosion rate units are given in Appendix X2. The expression of corrosion loss as a percentage of original weight is usually valueless.

8.3 Corrosion rates in milligrams per square decimetre per day may be expressed in terms of inches penetration per year (abbreviated ipy) by the following equation:

 $ipy = mdd \times (0.001437/d)$ 

where:

d = density of the metal, g/cm³.

8.4 It should be remembered always that any calculations of corrosion rates, such as "mdd" or "ipy," will be subject to error on account of nonuniform distribution of corrosion and changes of corrosion rates with time. In connection with the latter, it is often desirable to carry out the testing program so as to provide data from which curves can be plotted to illustrate changes in corrosion rates with time.

8.5 After reweighing, the specimens should be examined carefully and the average and maximum depths of pits, if any are present, determined by means of a calibrated microscope, or by direct measurement with a depth gage or sharp pointed micrometers. If the number of pits is very large, it should suffice to report the average depth of the ten deepest pits.

8.6 The depths of pits should be reported in thousandths of an inch for the test period. The size, shape, and distribution of pits should be noted. A distinction should be made between local attack or pitting that occurred underneath supporting devices and those pits that developed at the surfaces that had been exposed freely to the testing solution.

8.7 For special purposes it may be desirable to subject the specimen to simple bending tests and microscopical examination to determine whether any embrittlement or intergranular attack has occurred. Electrical resistance measurements of specimens of special type may be employed for studying these effects by comparing with specimens not subjected to test.

8.8 With suitable specimens, it may be possible to make quantitative mechanical tests comparing the exposed specimens with uncorroded specimens reserved for the purpose. By such means the effects of corrosion may be observed by measuring changes in mechanical properties.

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8.9 Under certain conditions the stainless steels are susceptible to stress-corrosion cracking. This effect may be studied by the exposure to the solution of specimens previously stressed to a known degree by some suitable method.

#### 9. Report

9.1 To the fullest extent that may be possible, the investigator should follow the recommendations embodied in the ASTM Manual on Quality Control of Materials.⁶ In any event the report should include the following information:

9.1.1 The chemical compositions of the metals and alloys tested (see 4.11),

9.1.2 The exact size, shape, and area of the specimen,

9.1.3 The forms and metallurgical conditions of the specimens,

9.1.4 The treatment used to prepare specimens for test,

9.1.5 The number of specimens of each material tested, whether each specimen was tested in a separate container or which specimens were tested in the same container,

9.1.6 The chemical composition of the testing solution and information as to how and to what extent the composition was held constant or how frequently the solution was replaced,

9.1.7 The temperature of the testing solution and the maximum variation in temperature during the test,

9.1.8 The degree of aeration of the solution in terms of cubic centimetres of air per litre of solution per minute and the maximum variation in this flow, or similar information for any gas or mixture of gases other than air. The type of aerator should also be described,

9.1.9 The velocity of relative movement between the test specimens and the solution and a description of how this movement was effected and controlled,

9.1.10 The volume of the testing solution,

9.1.11 The nature of the apparatus used for the test,

9.1.12 The duration of the test or of each part of it if made in more than one stage,

9.1.13 The method used to clean specimens after exposure and the extent of any error

⁶ Issued as Special Technical Publication 15-C. December 1957.

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introduced by this treatment,

9.1.14 The actual weight losses of the several specimens, depths of pits (plus notes on their size, shape and distribution, as by sketch), data on mechanical properties before and after

exposure if determined, results of microscopical examination or qualitative bend tests, and

9.1.15 Corrosion rates for individual specimens calculated in milligrams per square decimetre per day.

#### **APPENDIXES**

#### XI. METHOD FOR ELECTROLYTIC CLEANING OF CORROSION TEST SPECIMENS AFTER EXPOSURE

X1.1 After scrubbing to remove loosely attached corrosion products, treat the specimens as a cathode in hot, diluted sulfuric acid under the following conditions: .. .

Test solution	sulfuric acid (5 weight, %)
Thinbitor	2 mi organic innottor/ nire or solution
Anode	carbon
Cathode	test specimen
Cathode current density	20 A/dm ²
Temperature	165 F (74 C)
Exposure period	3 min

X1.2 After the electrolytic treatment, the specimen should be scrubbed. The weight losses of specimens 0.5 dm² in area treated by the method described have been found to be less than 0.0002 mg.

X1.3 Instead of using 2 ml of any proprietary inhibitor, about 0.5 g/litre of such inhibitors as diorthotolyl thiourea, quinoline ethiodide, beta-naphthol quinoline may be used.

X1.4 It should be noted that this electrolytic treatment may result in the redeposition of adherent metal from reducible corrosion products and thus lower the apparent weight loss. However, general experience has indicated that in most cases of corrosion in liquids the possible errors from this source are not likely to be serious.

#### **X2. CONVERSION FACTORS**

Multiply	Ву	To Obtain
Grams per square inch per hour	372 000	milligrams per square decimetre per day (mdd)
Grams per square metre per year	0.0274	milligrams per square decimetre per day (mdd)
Milligrams per square decimetre	0.0003277	ounces per square foot
Milligrams per square decimetre per day (mdd)	0.00000269	grams per square inch per hour
Milligrams per square decimetre per day (mdd) ¹	0.001437/density of metal in g/cm ³	penetration inches per year
Milligrams per square decimetre per day (mdd)	0.0001198/density of metal in g/cm ⁸	penetration inches per month
Milligrams per square decimetre per day (mdd)	36.5	grams per square metre per year
Milligrams per square decimetre per day (mdd)	0.00365/density of metal in g/cm ³	penetration centimetres per year
Milligrams per square decimetre per day (mdd)	0.00748	pounds per square foot per year
Ounces per square foot	3052	milligrams per square decimetre
Pounds per square foot per year	133.8	milligrams per square decimetre per day (mdd)

¹ Factors for converting milligrams per square decimetre per day to inches penetration per year, for different AISI types of stainless steels are given in Table X1.

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TABLE X1 Factors for Converting Milligrams per Square Decimetre per Day to Inches Penetration per Year for Different Types of Stainless Steel

AISI Type No.	Multiply Corrosion Rate in mg/dm ² day by indicated factor to get in. penetration per year
410-	0.000186
430	0.000186
446	0.000189
302	0.000182
304	0 000182
308	0.000182
309	0.000182
310	0.000182
316	0.000180
317	0.000180
321	0.000182
347	0.000180

By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

# Designation: B 117 – 73

American National Standard Z118.1 American National Standards Institute Endorsed by American Electroplaters' Society Endorsed by National Association of Metal Finshers Federation of Societies for Paint Technology Standard No. Ld 18-62

## Standard Method of SALT SPRAY (FOG) TESTING¹

This Standard is issued under the fixed designation B 117; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

This method has been approved by the Department of Defense to replace method 811.1 of Federal Test Method Standard No. 151b and for listing in DoD Index of Specifications and Standards. Future proposed revisions should be coordinated with the Federal Government through the Army Materials and Mechanics Research Center, Watertown, Mass. 02172.

#### 1. Scope

1.1 This method sets forth the conditions required in salt spray (fog) testing for specification purposes. Suitable apparatus which may be used to obtain these conditions is described in Appendix A1. The method does *not* prescribe the type of test specimen or exposure periods to be used for a specific product, nor the interpretation to be given to the results. Comments on the use of the test in research will be found in Appendix A2.

NOTE 1—This method is applicable to salt spray (fog) testing of ferrous and non-ferrous metals, and is also used to test inorganic and organic coatings, etc., especially where such tests are the basis for material or product specifications.

#### 2. Apparatus

2.1 The apparatus required for salt spray (fog) testing consists of a fog chamber, a salt solution reservoir, a supply of suitably conditioned compressed air, one or more atomizing nozzles, specimen supports, provision for heating the chamber, and necessary means of control. The size and detailed construction of the apparatus are optional, provided the conditions obtained meet the requirements of this method.

2.2 Drops of solution which accumulate on the ceiling or cover of the chamber shall not be permitted to fall on the specimens being tested.

2.3 Drops of solution which fall from the specimens shall not be returned to the solution reservoir for respraying.

2.4 Material of construction shall be such that it will not affect the corrosiveness of the fog.

#### 3. Test Specimens

3.1 The type and number of test specimens to be used, as well as the criteria for the evaluation of the test results, shall be defined in the specifications covering the material or product being tested or shall be mutually agreed upon by the purchaser and the seller.

#### 4. Preparation of Test Specimens

4.1 Metallic and metallic-coated specimens shall be suitably cleaned. The cleaning method shall be optional depending on the nature of the surface and the contaminants, except that it shall not include the use of abrasives other than a paste of pure magnesium oxide nor of solvents which are corrosive or will deposit either corrosive or protective films. The use of a nitric acid solution for the chemical cleaning, or passivation, of stainless steel specimens is permissible when agreed upon by the purchaser and the seller. Care shall be taken that specimens are not recontaminated after cleaning by excessive or careless handling.

4.2 Specimens for evaluation of paints and other organic coatings shall be prepared in accordance with applicable specification(s) for the material(s) being tested, or as agreed upon by the purchaser and supplier. Otherwise, the test specimens shall consist of steel meeting the requirements of ASTM Methods D 609 for Preparation of Steel Panels for Testing

¹ This method is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals, and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

Current edition approved March 29, 1973. Published June 1973. Originally published as B 117 - 39 T. Last previous edition B 117 - 64.

Paint, Varnish, Lacquer, and Related Products,² and shall be cleaned and prepared for coating in accordance with applicable procedure of Method D 609.

4.3 Specimens coated with paints or nonmetallic coatings shall not be cleaned or handled excessively prior to test.

4.4 Whenever it is desired to determine the development of corrosion from an abraded area in the paint or organic coating, a scratch or scribed line shall be made through the coating with a sharp instrument so as to expose the underlying metal before testing. The conditions of making the scratch shall be as defined in ASTM Method D 1654, Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments,² unless otherwise agreed upon between the purchaser and seller.

4.5 Unless otherwise specified, the cut edges of plated, coated, or duplex materials and areas containing identification marks or in contact with the racks or supports shall be protected with a suitable coating stable under the conditions of the test, such as ceresin wax.

NOTE 2—Should it be desirable to cut test specimens from parts or from preplated, painted, or otherwise coated steel sheet, the cut edges shall be protected by coating them with paint, wax, tape, or other effective media so that the development of a galvanic effect between such edges and the adjacent plated or otherwise coated metal surfaces, is prevented.

#### 5. Position of Specimens During Test

5.1 The position of the specimens in the salt spray chamber during the test shall be such that the following conditions are met:

5.1.1 Unless otherwise specified, the specimens shall be supported or suspended between 15 and 30 deg from the vertical and preferably parallel to the principal direction of horizontal flow of fog through the chamber, based upon the dominant surface being tested.

5.1.2 The specimens shall not contact each other or any metallic material or any material capable of acting as a wick.

5.1.3 Each specimen shall be so placed as to permit free settling of fog on all specimens.

5.1.4 Salt solution from one specimen shall not drip on any other specimen.

NOTE 3—Suitable materials for the construction or coating of racks and supports are glass, rubber, plastic, or suitably coated wood. Bare metal shall not be used. Specimens shall preferably be supported from the bottom or the side. Slotted wooden

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strips are suitable for the support of flat panels. Suspension from glass hooks or waxed string may be used as long as the specified position of the specimens is obtained, it necessary by means of secondary support at the bottom of the specimens.

#### 6. Salt Solution

6.1 The salt solution shall be prepared by dissolving 5  $\pm$  1 parts by weight of sodium chloride in 95 parts of distilled water or water containing not more than 200 ppm of total solids. The salt used shall be sodium chloride substantially free of nickel and copper and containing on the dry basis not more than 0.1 percent of sodium iodide and not more than 0.3 percent of total impurities. Some salts contain additives that may act as corrosion inhibitors; careful attention should be given to the chemical content of the salt. By agreement between purchaser and seller, analysis may be required and limits established for elements or compounds not specified in the chemical composition given above.

6.2 The pH of the salt solution shall be such that when atomized at 35 C (95 F) the collected solution will be in the pH range of 6.5 to 7.2 (Note 4). Before the solution is atomized it shall be free of suspended solids (Note 5). The pH measurement shall be made electrometrically at 25 C (77 F) using a glass electrode with a saturated potassium chloride bridge in accordance with Method E 70, Test for pH of Aqueous Solutions with the Glass Electrode³; or colorimetrically using bromothymol blue as indicator, or short range pH paper which reads in 0.2 or 0.3 of a pH unit (Note 6).

NOTE 4—Temperature affects the pH of a salt solution prepared from water saturated with carbon dioxide at room temperature and pH adjustment may be made by the following three methods:

(1) When the pH of a salt solution is adjusted at room temperature, and atomized at 35 C (95 F), the pH of the collected solution will be higher than the original solution due to the loss of carbon dioxide at the higher temperature. When the pH of the salt solution is adjusted at room temperature, it is therefore necessary to adjust it below 6.5 so the collected solution after atomizing at 35 C (95 F) will meet the pH limits of 6.5 to 7.2. Take about a 50-ml sample of the salt solution as prepared at room temperature, boil gently for 30 s, cool, and determine the pH. When the pH of the salt solution is adjusted to 6.5 to 7.2 by this procedure, the pH of the atomized and collected solution at 35 C (95 F) will come within this range.

² Annual Book of ASTM Standards, Part 21.

^a Annual Book of ASTM Standards, Parts 16, 22, 30.

(2) Heating the salt solution to boiling and cooling to 95 F or maintaining it at 95 F for approximately 48 h before adjusting the pH produces a solution the pH of which does not materially change when atomized at 35 C (95 F).

(3) Heating the water from which the salt solution is prepared to 35 C (95 F) or above, to expel carbon dioxide, and adjusting the pH of the salt solution within the limits of 6.5 to 7.2 produces a solution the pH of which does not materially change when atomized at 35 C (95 F).

NOTE 5-The freshly prepared salt solution may be filtered or decanted before it is placed in the reservoir, or the end of the tube leading from the solution to the atomizer may be covered with a double layer of cheesecloth to prevent plugging of the nozzle.

NOTE 6-The pH can be adjusted by additions of dilute cp hydrochloric acid or cp sodium hydroxide solutions.

#### 7. Air Supply

7.1 The compressed air supply to the nozzle or nozzles for atomizing the salt solution shall be free of oil and dirt (Note 7) and maintained between 69 and 172 kN/m² (10 and 25 psi) (Note 8).

NOTE 7-The air supply may be freed from oil and dirt by passing it through a water scrubber or at least 610 mm (2 ft) of suitable cleaning material such as asbestos, sheep's wool, excelsior, slag wool, or activated alumina.

NOTE 8—Atomizing nozzles may have a "critical pressure" at which an abnormal increase in the corrosiveness of the salt fog occurs. If the "critical pressure" of a nozzle has not been established with certainty, control of fluctuation in the air pressure within plus or minus  $0.7 \text{ kN/m}^2$  (0.1 psi), by installation of a suitable pressure regulator valves minimizes the possibility that the nozzle will be operated at its "critical pressure."

#### 8. Conditions in the Salt Spray Chamber

8.1 Temperature-The exposure zone of the salt spray chamber shall be maintained at 35 + 1.1 - 1.7 C (95 + 2 - 3 F). The temperature within the exposure zone of the closed cabinet shall be recorded at least twice a day at least 7 h apart (except on Saturdays, Sundays, and holidays when the salt spray test is not interrupted for exposing, rearranging, or removing test specimens or to check and replenish the solution in the reservoir).

NOTE 9-A suitable method to record the temperature is by a continuous recording device or by a thermometer which can be read from outside the closed cabinet. The recorded temperature must be obtained with the salt spray chamber closed to avoid a false low reading because of wet-bulb effect when the chamber is open.

8.2 Atomization and Quantity of Fog-At least two clean fog collectors shall be so

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> placed within the exposure zone that no drops of solution from the test specimens or any other source shall be collected. The collectors shall be placed in the proximity of the test specimens, one nearest to any nozzle and the other farthest from all nozzles. The fog shall be such that for each 80 cm² of horizontal collecting area there will be collected in each collector from 1.0 to 2.0 ml of solution per hour based on an average run of at least 16 h (Note 10). The sodium chloride concentration of the collected solution shall be 5  $\pm$  1 weight percent (Note 11). The pH of the collected solution shall be 6.5 to 7.2. The pH measurement shall be made electrometrically or colorimetrically using bromothymol blue as the indica-

> NOTE 10-Suitable collecting devices are glass funnels with the stems inserted through stoppers into graduated cylinders, or crystallizing dishes. Funnels and dishes with a diameter of 10 cm have an area of about 80 cm².

> NOTE 11-A solution having a specific gravity of 1.0255 to 1.0400 at 25 C (77 F) will meet the concentration requirement. The concentration may also be determined as follows: Dilute 5 ml of the collected solution to 100 ml with distilled water and mix thoroughly; pipet a 10-ml aliquot into an evaporating dish or casserole; add 40 ml of distilled water and 1 ml of 1 percent potassium chromate solution (chloride-free) and titrate with 0.1 N silver nitrate solution to the first appearance of a permanent red coloration. A solution that requires between 3.4 and 5.1 ml of 0.1 N silver nitrate solution will meet the concentration requirements.

> 8.3 The nozzle or nozzles shall be so directed or baffled that none of the spray can impinge directly on the test specimens.

#### 9. Continuity of Test

9.1 Unless otherwise specified in the specifications covering the material or product being tested, the test shall be continuous for the duration of the entire test period. Continuous operation implies that the chamber be

^{*} Registered U. S. Patent Office.

^{*} The Nullmatic pressure regulator (or equivalent) man-ufactured by Moore Products Co., H and Lycoming Sts., Philadelphia, Pa. 1912.4, is suitable for this purpose. * It has been observed that periodic fluctuations in air

pressure of  $\pm 3.4$  kN/m² (0.5 psi) resulted in about a two-fold increase in the corrosivity of the fog from a nozzle but increase in the corrosivity of the log from a nozzle which was being operated at an average pressure of 110 kN/m² (16 psi). Controlling the fluctuations within  $\pm 0.7$  kN/m² (0.1 psi), however, avoided any increase in the corrosivity of the salt fog. See Darsey, V. M. and Cavanagh, W. R., "Apparatus and Factors in Salt Fog Testing," *Proceedings*, ASTEA, Am. Soc. Testing Mats., Vol. 49, 1048 - 153. 48, 1948, p. 153.

closed and the spray operating continuously except for the short daily interruptions necessary to inspect, rearrange, or remove test specimens; to check and replenish the solution in the reservoir, and to make necessary recordings as described in Section 8. Operations shall be so scheduled that these interruptions are held to a minimum.

#### 10. Period of Test

10.1 The period of test shall be as designated by the specifications covering the material or product being tested or as mutually agreed upon by the purchaser and the seller.

NOTE 12—Recommended exposure periods are to be as agreed upon by the purchaser and seller, but exposure periods of multiples of 24 h are suggested.

#### 11. Cleaning of Tested Specimens

11.1 Unless otherwise specified in the specifications covering the material or product being tested, specimens shall be treated as follows at the end of the test:

11.1.1 The specimens shall be carefully removed.

11.1.2 Specimens may be gently washed or dipped in clean running water not warmer than 38 C (100 F) to remove salt deposits from their surface, and then immediately dried. Drying shall be accomplished with a stream of clean, compressed air.

#### 12. Evaluation of Results

12.1 A careful and immediate examination shall be made for the extent of corrosion of the dry test specimens or for other failure as required by the specifications covering the

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material or product being tested or by agreement between the purchaser and the seller.

#### 13. Records and Reports

13.1 The following information shall be recorded, unless otherwise prescribed in the specifications covering the material or product being tested:

13.1.1 Type of salt and water used in preparing the salt solution,

13.1.2 All readings of temperature within the exposure zone of the chamber,

13.1.3 Daily records of data obtained from each fog-collecting device including the following:

13.1.3.1 Volume of salt solution collected in milliliters per hour per 80 cm²,

13.1.3.2 Concentration or specific gravity at 35 C (95 F) of solution collected, and

13.1.3.3 pH of collected solution.

13.4 Type of specimen and its dimensions, or number or description of part,

13.5 Method of cleaning specimens before and after testing,

13.6 Method of supporting or suspending article in the salt spray chamber,

13.7 Description of protection used as required in 4.5,

13.8 Exposure period,

13.9 Interruptions in test, cause and length of time, and

13.10 Results of all inspections.

NOTE 13—If any of the atomized salt solution which has not contacted the test specimens is returned to the reservoir, it is advisable to record the concentration or specific gravity of this solution also.

#### APPENDIXES

#### A1. CONSTRUCTION OF APPARATUS

#### A1.1 Cabinets

A1.1.1 Standard salt-spray cabinets are available from several suppliers, but certain pertinent accessories are required before they will function according to this method and provide consistent control for duplication of results.

A1.1.2 The salt spray cabinet consists of the basic chamber, an air-saturator tower, a salt solution reservoir, atomizing nozzles, specimen supports, provisions for heating the chamber, and suitable controls for maintaining the desired temperature.

A1.1.3 Accessories such as a suitable adjustable baffle or central fog tower, automatic level control for the salt reservoir, and automatic level control for the air-saturator tower are pertinent parts of the apparatus.

A1.1.4 The cabinet should be of sufficient size to test adequately the desired number of parts without overcrowding. Small cabinets have been found difficult to control and those of less than 0.43-m³ (15-ft³) capacity should be avoided.

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A1.1.5 The chamber may be made of inert materials such as plastic, glass, or stone, but most preferably is constructed of metal and lined with impervious plastics, rubber, or epoxy-type materials or equivalent.

#### A1.2 Temperature Control

A1.2.1 The maintenance of temperature within the salt chamber can be accomplished by several methods. It is generally desirable to control the temperature of the surroundings of the salt spray chamber and to maintain it as stable as possible. This may be accomplished by placing the apparatus in a constant-temperature room, but may also be achieved by surrounding the basic chamber of a jacket containing water or air at a controlled temperature.

A1.2.2 The use of immersion heaters in an internal salt-solution reservoir or of heaters within the chamber is detrimental where heat losses are appreciable, because of solution evaporation and radiant heat on the specimens.

A1.2.3 All piping which contacts the salt solution or spray should be of inert materials such as plastic. Vent piping should be of sufficient size so that a minimum of back pressure exists and should be installed so that no solution is trapped. The exposed end of the vent pipe should be shielded from extreme air currents that may cause fluctuation of pressure or vacuum in the cabinet.

#### A1.3 Spray Nozzles

A1.3.1 Satisfactory nozzles may be made of hard rubber, plastic, or other inert materials. The most commonly used type is made of plastic. Nozzles calibrated for air consumption and solution atomized are available. The operating characteristics of a typical nozzle are given in Table A1.

A1.3.2 It can readily be seen that air consumption is relatively stable at the pressures normally used, but a marked reduction in solution sprayed occurs if the level of the solution is allowed to drop appreciably during the test. Thus, the level of the solution in the salt reservoir must be maintained automatically to ensure uniform fog delivery during the test.⁷

A1.3.3 If the nozzle selected does not atomize the salt solution into uniform droplets, it will be necessary to direct the spray at a baffle or wall to pick up the larger drops and prevent them from impinging on the test specimens. Pending a complete understanding of air-pressure effects, etc., it is important that the nozzle selected shall produce the desired condition when operated at the air pressure selected. Nozzles are not necessarily located at one end, but may be placed in the center and can also be directed vertically up through a suitable tower.

#### A1.4 Air for Atomization

A1.4.1 The air used for atomization must be free of grease, oil, and dirt before use by passing through well-maintained filters. Room air may be compressed, heated, humidified, and washed in a water-sealed rotary pump, if the temperature of the water is suitably controlled. Otherwise cleaned air may be introduced into the bottom of a tower filled with water, through a porous stone or multiple nozzles. The level of the water must be maintained automatically to ensure adequate humidification. A chamber operated according to this method and Appendix will have a relative humidity between 95 and 98 percent. Since salt solutions from 2 to 6 percent will give the same results (though for uniformity the limits are set at 4 to 6 percent), it is preferable to saturate the air at temperatures well above the chamber temperature as insurance of a wet fog. Table A2 shows the temperatures, at different pressures, that are required to offset the cooling effect of expansion to atmospheric pressure.

A1.4.2 Experience has shown that most uniform spray chamber atmospheres are obtained by increasing the atomizing air temperature sufficiently to offset heat losses, except those that can be replaced otherwise at very low-temperature gradients.

#### A1.5 Types of Construction

A1.5.1 A modern laboratory cabinet is shown in Fig. A1. Walk-in chambers are not usually constructed with a sloping ceiling due to their size and location. Suitably located and directed spray nozzles avoid ceiling accumulation and drip. Nozzles may be located at the ceiling, or 0.91 m (3 ft) from the floor directed upward at 30 to 60 deg over a passageway. The number of nozzles depends on type and capacity and is related to the area of the test space. A 11 to 19-dm³ (3 to 5-gal) reservoir is required within the chamber, with the level controlled. The major features of a walk-in type cabinet, which differs significantly from the laboratory type, are illustrated in Fig. A2. Construction of a plastic nozzle, such as is furnished by several suppliers, is shown in Fig. A3.

#### A2. USE OF THE SALT SPRAY (FOG) TEST IN RESEARCH

A2.1 The detailed requirements of this method are primarily for quality acceptance and should not be construed as the optimum conditions for research studies. The test has been used to a considerable extent for the purpose of comparing different materials or finishes with an acceptable standard. The recent elimination of many cabinet variables and the improvement in controls have made the three ASTM Salt Spray Tests: Method B 117, Method B 287, Acetic Acid-Salt Spray (Fog) Testing,⁶ and Method B 368, for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS),⁶ into useful tools for many industrial and military production

⁷ A suitable device for maintaining the level of liquid in, either the saturator tower, or reservoir of test solution may be designed by a local engineering group, or may be purchased from manufacturers of test cabinets as an accessory.

^{*} Annual Book of ASTM Standards, Part 7.

and qualification programs.

A2.2 The test has been used to a considerable extent for the purpose of comparing different materials or finishes. It should be noted that there is seldom a direct relation between salt spray (fog) resistance and resistance to corrosion in other media, because the chemistry of the reactions, including the formation of films and their protective value, frequently varies greatly with the precise conditions encountered. Informed personnel are aware of the erratic composition of basic alloys, the possibility of wide variations in quality and thickness of plated items produced on the same racks at the same time, and the consequent need for a mathematical determination of the number of specimens required to constitute an adequate sample for test purposes. In this connection it is well to point out that Method B117 is not applicable to the study or testing of decorative chromium plate (nickel-chromium or copper-nickel-chromium) on steel or on zinc-base die castings or of cadmium plate on steel. For this purpose Methods B 287 and B 368 are available, which are also considered by some to be superior for comparison of chemically-treated aluminum

TABLE A1 Operating Characteristics of Typical Spray Nozzle

Siphon		Air F liters	low, ∕min	_	Con	Solu	ution ion,	m1/h
Height, in.	Air Pressure, psi		Air Pressu		isure,	ure, psi		
	5	10	15	20	5	10	15	20
4	19	26.5	31.5	36	2100	3840	4584	5256
8	19	26.5	31.5	36	636	2760	3720	4320
12	19	26.5	31.5	36	0	1380	3000	3710
16	19	26.6	31.5	36	0	780	2124	2904

Sinkan	Air Flow, dm [*] /min				Solution Consumpt cm ³ /h			ption,
Height	ght n Air Pressure, kN/m ²			Air Pressure. kN/m ²				
	34	69	103	138	34	69	103	138
10 20 30 40	19 19 19 19	26.5 26.5 26.5 26.6	31.5 31.5 31.5 31.5 31.5	36 36 36 36	2100 636 0 0	3840 2760 1380 780	4584 3720 3000 2124	5256 4320 3710 2904

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(chromated, phosphated, or anodized), although final conclusions regarding the validity of test results related to service experience have not been reached. Method B117 is considered to be most useful in estimating the relative behavior of closely related materials in marine atmospheres, since it simulates the basic conditions with some acceleration due to either wetness or temperature or both.

A2.3 When a test is used for research, it may prove advantageous to operate with a different solution composition or concentration or at a different temperature. In all cases, however, it is desirable to control the temperature and humidity in the manner specified, and to make certain that the composition of the settled fog and that of the solution in the reservoir are substantially the same. Where differences develop, it is necessary to control conditions so that the characteristics of the settled fog meet the specified requirements for the atmosphere.

A2.4 Material specifications should always be written in terms of the standard requirements of the appropriate salt-spray method, thereby making it possible to test a variety of materials from different sources in the same equipment.

Test a	t 95 F	auou	01	
	Α	ir Pre	ssure.	psi
	12	14	16	18
Temperature, deg F	114	117	119	121
	Air	Pressu	ire, kN	i∕m⁴
	83	96	110	124
Temperature, deg C	46	47	48	49

#### TABLE A2 Temperature and Pressure Requirements for Operation of Test at 95 F

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- A
- Angle of lid, 90 to 125 deg Thermometer and thermostat for controlling heater (Item No. 8) in base
- Automatic water levelling device 2 3
- Humidifying tower
- 4 Automatic temperature regulator for controlling heater (Item No. 5)
- 5 ----Immersion heater, non-rusting
- Air inlet, multiple openings
  Air tube to spray nozzle
  Strip heater in base б
- 7
- 8 ā
- Hinged top, hydraulically operated, or counterbalanced 10 -
- Brackets for rods supporting specimens, or test table
- 11 Internal reservoir
- 12 Spray nozzle above reservoir, suitably designed, located, and baffled 12A Spray nozzle housed in dispersion tower located preferably in center of cabinet 13
- Water Seal 14 -
- Combination drain and exhaust. Exhaust at opposite side of test space from spray nozzle (Item 12), but preferably in combination with drain, waste trap, and forced draft waste pipe (Items 16, 17, and 19). Complete separation between forced draft waste pipe (Item 17) and combination drain and exhuast (Items 14 and 19) 16 -
- to avoid undesirable suction or back pressure. 17 — Forced draft waste pipe.
   18 — Automatic levelling device for reservoir
   19 — Waste trap

- 20 Air space or water jacket
- 21 Test table or rack, well below roof area

FIG. A1 Typical Salt Spray Cabinet.



NOTE-The controls are the same, in general as for the laboratory cabinet (Fig. A1), but are sized to care for the larger cube. The chamber has the following features: (1) Heavy insulation.

- (2) Refrigeration door with drip rail, or pressure door
- with drip radi, inward-sloping sill,
  (3) Low-temperature auxiliary heater, and
  (4) Duck boards on floor, with floor sloped to combination drain and air exhaust.

## FIG. A2 Walk-in Chamber, 1.5 by 2.4 mm (5 by 8 ft) and Upward in Over-all Size.



By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

# Designation: G 1 - 72

## Standard Recommended Practice for PREPARING, CLEANING, AND EVALUATING CORROSION TEST SPECIMENS¹

This Standard is issued under the fixed designation G 1; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

#### 1. Scope

1.1 This recommended practice gives suggested procedures for preparing bare, solid metal specimens for laboratory corrosion tests, for removing corrosion products after the test has been completed, and for evaluating the corrosion damage that has occurred. Emphasis is placed on procedures related to the evaluation of corrosion by mass-loss and pitting measurements.

#### 2. Applicable Documents

#### 2.1 ASTM Standards:

- A 262, Recommended Practice for Detecting Susceptibility to Intergranular Attack in Stainless Steels.²
- A 279, Total Immersion Corrosion Test of Stainless Steels.²
- D1384, Corrosion Test for Engine Antifreezes in Glassware.³

#### 3. Methods for Preparing Specimens for Test

3.1 Surface Condition:

3.1.1 For laboratory corrosion tests that simulate exposure to service environments, a commercial surface, closely resembling the one that would be used in service, will yield the most significant results.

3.1.2 For more searching tests of either the metal or the environment, standard surface finishes may be preferred. A suitable procedure might be:

3.1.2.1 Degrease in an organic solvent or hot alkaline cleaner.

NOTE 1-Hot alkalies and chlorinated solvents may attack some metals (for example, aluminum).

NOTE 2-Ultrasonic cleaning may be beneficial in both pre-test and post-test cleaning procedures.

3.1.2.2 Pickle in an appropriate solution (in some cases the chemical cleaners described in Section 5 will suffice) if oxides or tarnish are present.

3.1.2.3 Abrade with a slurry of an appropriate abrasive or with an abrasive paper (see Methods A 262 and A 279 and Recommended Practice D 1384). The edges as well as the faces of the specimens should be abraded to remove burrs.

3.1.2.4 Rinse thoroughly and dry.

3.2 Metallurgical Condition-When specimen preparation changes the metallurgical condition of the metal, other methods should be chosen or the metallurgical condition must be corrected by subsequent treatment. For example, shearing a specimen to size will cold work and may possibly fracture the edges. Edges should be machined or the specimen annealed.

3.3 The clean, dry specimens should be measured and weighed. Dimensions determined to the third significant figure and mass determined to the fifth significant figure are suggested.

#### 4. Method for Electrolytic Cleaning After Testing

4.1 Electrolytic cleaning is a satisfactory method for many common metals.

4.1.1 The following method is typical; after

² Annual Book of ASTM Standards, Part 3. ³ Annual Book of ASTM Standards, Part 22.

¹This recommended practice is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.05 on Laboratory Corrosion Tests.

Current edition approved May 30, 1972. Published July 1972. Originally published as G 1 - 67. Last pre-vious edition G 1 - 67.  $^{2}Annual Book of ASTM Standards Bart 3$ 

scrubbing to remove loosely attached corrosion products, electrolyze the specimen as follows:

Sulfuric acid (H ₂ SO ₄ ,	28 ml
sp gr 1.84)	
Organic inhibitor	2 ml (see Note 3)
Water to make	1 liter
Temperature	75 C (167 F)
Time	3 min
Anode	carbon or lead (see Note 4)
Cathode	test specimen
Current density	20 A/dm ²

NOTE 3—Instead of using 0.2 volume percent of any proprietary inhibitor, about 0.5 g/liter of such inhibitors as diorthotolyl thiourea, quinoline ethiodide, or betanaphthol quinoline may be used.

NOTE 4—If lead anodes are used, lead may deposit on the specimen and cause an error in the mass loss. If the specimen is resistant to nitric acid, the lead may be removed by a flash dip in 1+1 nitric acid. Except for this possible source of error, lead is preferred as an anode as it gives more efficient corrosion-product removal.

4.2 It should be noted that this electrolytic treatment may result in the redeposition of metal, such as copper, from reducible corrosion products and, thus, lower the apparent mass loss.

#### 5. Methods for Chemical Cleaning After Testing

NOTE 5: Caution—These methods may be hazardous to personnel. They should not be carried out by the uninitiated or without professional supervision.

5.1 Copper and Nickel Alloys-Dip in:

Hydrochloric acid (HCl, sp gr 1.19) or	500 ml
Sulfuric acid (H ₂ SO ₄ , sp gr 1.84)	100 mi
Water to make	1 liter
Temperature	room
Time	1 to 3 min

5.2 Aluminum Alloys-Dip in:

Temperature

Time

Chromic acid (CrO ₃ )	20 g
Phosphoric acid (H ₃ PO ₄ , sp gr 1.69)	50 ml
Water to make	1 liter
Temperature	80 C (176 F)
Time	5 to 10 min
5.2.1 If a film remains, dip in:	
Nitric acid (HNO ₁ , sp gr 1.42) Time	l min
5.2.2 Repeat CrO, dip.	
5.2.2.1 Nitric acid alone may there are no deposits. 5.3 <i>Tin Alloys</i> —Dip in:	be used if
Trisodium phosphate (Na,PO,) Water to make	150 g Liter

boiling

10 min

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5.4 Lead Alloys-Suitable methods include:

5.4.1 Preferably, use the electrolytic cleaning procedure of Section 4.

5.4.2 Dip in:

•	
Acetic acid (99.5 percent)	10 ml
Water to make	1 liter
Temperature	boiling
Time	5 min
5.4.3 Alternatively dip in:	

Ammonium acetate50 gWater to maket literTemperaturehotTime5 min

5.4.3.1 This removes lead oxide (PbO) and lead sulfate (PbSO₄).

5.5 Zinc—The following methods are suitable:

5.5.1 Dip in:

Ammonium hydroxide (NH ₄ OH,	150 ml
Water to make	1 liter
Temperature	room
Fime	several minutes
5.5.2 Then dip in:	

Chromic acid (CrO ₁ )	50 g
Silver nitrate (AgNO ₁ )	10 g
Water to make	l liter
Temperature	boiling
Time	15 to 20 s

NOTE 6—In making up the chromic acid solution, it is advisable to dissolve the silver nitrate separately and add it to the boiling chromic acid to prevent excessive crystallization of the silver chromate. The chromic acid must be free from sulfate to avoid attack on the zinc.

5.5.2 Dip in:	
Hydriodic acid (HI, sp gr 1.5)	85 ml
Water to make	1 liter
Temperature	room
Time	15 s

5.5.2.1 This procedure dissolves a little zinc and corrections must be made as noted in 6.1. 5.6 *Magnesium Alloys*—Dip in:

Chromic acid (CrO ₁ )	150 g
Silver chromate (Ag ₂ CrO ₄ )	10 g
Water to make	1 liter
Temperature	boiling
Time	1 min

#### 5.7 Iron and Steel-Suitable methods are:

5.7.1 The hot sodium hydride method is excellent for cleaning iron and steel both from the point of view of ease of removal of corrosion products and minimum attack on the

metal.4 Because of the hazard involved and the somewhat more sophisticated equipment required, other methods may be preferred. An alternative choice is electrolytic cleaning (see Section 4).

5.7.2 Dip in Clarke's solution:

l liter
20 g
50 g
room
up to 25 mi

5.7.2.1 Solution should be vigorously stirred or the specimen should be rubbed with

a nonabrasive implement of wood or rubber.

5.7.3 Dip in:

Sulfuric acid (H ₂ SO ₄ , sp gr 1.84)	100 ml
Organic inhibitor	1.5 ml
Water to make	l liter
Temperature	50 C (120 F)

5.8 Stainless Steels:

5.8.1 Methods in 5.7.1 are also applicable 5.8.2 Dip in:

Nitric acid (HNO ₃ , sp gr 1.42)	100 mi
Water to make	1 liter
Temperature	60 C (140 F)
Time	20 min

5.8.3 Alternatively dip in:

Ammonium citrate	150 g
Water to make	l liter
Temperature	70 C (158 F)
Time	10 to 60 min

5.9 In place of chemical cleaning, use a brass scraper or brass bristle brush, or both, followed by scrubbing with a wet bristle brush and fine scouring powder. However, this method may not remove all the products from pits.

NOTE 7-Such vigorous mechanical cleaning is applicable when mass losses are large and hence errors in mass loss will produce only small errors in corrosion rates. Blank corrections will be difficult to apply.

5.10 In all the foregoing methods, 'specimens should be rinsed following cleaning and scrubbed lightly with a bristle brush under running water. The cleaning dip may be repeated as necessary. After the final rinse, specimens should be dried and weighed.

#### 6. Calculation of Corrosion Rate

6.1 Whatever cleaning method is used, the possibility of removal of solid metal is present; this results in error in the determina-

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tion of the corrosion rate. To check this, one or more cleaned and weighed specimens may be recleaned by the same method and reweighed. Loss due to this second weighing may be used as an approximate correction to the first one (see Appendix A2 for a more exact method).

6.2 The initial total surface area of the specimen (making allowances for the change in area due to mounting holes) and the mass lost during the test are determined. The average corrosion rate may then be obtained as follows.

Corrosion rate =  $(K \times W)/(A \times T \times D)$ 

where:

Κ = a constant (see 6.2.1),

Т = time of exposure in hours to the nearest 0.01 h,

 $A = \text{area in } \text{cm}^2 \text{ to the nearest } 0.01 \text{ cm}^2$ .

W = mass loss in g, to nearest 1 mg, and

 $D = \text{density in } g/\text{cm}^3 \text{ (see Appendix A1).}$ 

6.2.1 Many different units are used to express corrosion rates. Using the above units for T, A, W, and D the corrosion rate can be calculated in a variety of units with the following appropriate value of K:

Corrosion Rate Units Desired	Constant (K) in Corrosion Rate Equation
mils per year (mpy)	$3.45 \times 10^{6}$
inches per year (ipy)	$3.45 \times 10^{3}$
inches per month (ipm)	$2.87 \times 10^{2}$
millimeters per year (mm/y)	$8.76 \times 10^{4}$
micrometers per year $(\mu m/y)$	$8.76 \times 10^{7}$
picometers per second (pm/s)	$2.78 \times 10^{6}$
grams per square meter per hour (g/m ² ·h)	$1.00 \times 10^4 \times D^a$
milligrams per square decimeter per day (mdd)	$2.40  imes 10^{s}  imes D^{a}$
micrograms per square meter per second ( $\mu g/m^2 \cdot s$ )	$2.78  imes 10^{s}  imes D^{a}$

^a Density is not needed to calculate the corrosion rate in these units; the density in the constant K cancels out the density in the corrosion rate equation.

NOTE 8-If desired, these constants may also be used to convert corrosion rates from one set of units to another. To convert a corrosion rate in units X to a rate in units Y, multiply by  $K_Y/K_X$  for example:

 $15 \text{ mpy} = 15 \times (2.78 \times 10^6) / (3.45 \times 10^6) \text{ pm/s}$ 

6.3 Corrosion rates calculated from mass

^{*}Technical Information Bulletin SP29-370 "DuPont Sodium Hydride Descaling Process Operating Instruc-tions,'' available from E. I. duPont de Nemours & Co. (Inc.), Electrochemicals Dept., Wilmington, Del. 19898.

losses can be misleading when deterioration is highly localized, as in pitting or crevice corrosion. If corrosion is in the form of pitting, it may be measured with a depth gage or micrometer calipers with pointed anvils. Microscopical methods will determine pit depth by focusing from top to bottom of the pit, when it is viewed from above (using a calibrated focusing knob) or by examining a section that has been mounted and metallographically polished. The pitting factor is the ratio of the deepest metal penetration to the average metal penetration (as measured by mass loss).

6.4 Other methods of assessing corrosion damage are:

6.4.1 Appearance—The degradation of appearance by rusting, tarnishing, or oxidation.

6.4.2 Mechanical Properties—An apparent loss in tensile strength will result if the crosssectional area of the specimen (measured before exposure to the corrosive environment) is

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reduced by corrosion. Loss in tensile strength will result if a metasomatic change, such as parting has taken place. Loss in tensile strength and elongation will result from localized attack, such as cracking.

6.4.3 *Electrical Properties*—Loss in apparent conductivity will result from cracking or pitting.

6.4.4 Microscopical Examination—Parting, exfoliation, cracking, or intergranular attack may be measured by metallographic examination of suitably prepared sections.

#### 7. Report

7.1 The report should include the compositions and sizes of specimens, their metallurgical conditions, surface preparations, and post-corrosion cleaning methods, as well as measures of corrosion damage such as corrosion rates (calculated from mass losses), maximum depths of pitting, or losses in mechanical properties.

#### APPENDIXES

#### A1. DENSITIES FOR A VARIETY OF METALS AND ALLOYS

	Density		Density
Aluminum Alloys	g/cm ³	Ferrous Metals	g/cm³
1100-3004	2 72	Gray cast iron	7.20
1100, 5004	2.72	Carbon steel	7.86
1199, 5005, 5557, 0001, 0002, 0070, 0101	2.70	Silicon iron	7.00
2024	2.77	Low alloy steels	7.85
2217, /1/0	2.81	Stainless steels:	
5005, 7079	2.74	Types 201, 202, 302, 304, 304L, 321	7.94
5050 5454	2.09	Types 309, 310, 311, 316, 316L, 317,	7.98
2022, 2424 2022, 2022, 2124, 2454	2.08	329, 330	
3083, 3086, 3134, 3436	2.00	Type 347	8.03
/0/5	2.80	Type 410	7.70
Copper Alloys		Type 430	7.72
Copper	8.94	Type 446	7.65
Brasses:		Type 502	7.82
Commercial bronze 220	8.80	Durimet 20	8.02
Red brass 230	8.75	Carpenter Stainless No. 20 Ch-3	8.05
Cartridge brass 260	8.52	carpenter stantess fro. 20 co p	
Muntz metal 280	8.39		
Admiralty 442, 443, 444, 445	8.52	Lead	
Aluminum brass 687	8.33	Antimonial	10.80
Bronzes:		Chemical	11.33
Aluminum bronze, 5 percent 608	8.16		
Aluminum bronze, 8 percent 612	7.78	Nickel Alloys	
Composition M	8.45	Nickel 200	8.89
Composition G	8.77	Monel Alloy 400	8.84
Phosphor bronze, 5 percent 510	8.86	Inconel Alloy 600	8.51
Phosphor bronze, 10 percent 524	8.77	Incoloy Alloy 825	8.14
85-5-5-5	8.80	Illium G	8.31
Silicon bronze 655	8.52	Hastelloy B	9.24
Conper nickels 706, 710, 715	8.94	Hastellov C	8.93
Nickel silver 752	8.75	Hastellov G	8.27
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Other Metals g/cm ³ Other Metals g/cm ³ Other Metals g/cm ³	nsity
Magnesium 174 Tin 7	cm *
1./4 In /.	.30
Molybdenum 10.22 Titanium 4.	.54
Platinum 21.45 Zinc 7.	.13
Silver 10.49 Zirconium 6.	.53
Tantalum 16.60	

## A2. METHOD FOR DETERMINING MASS LOSS WHERE CLEANING MAY ATTACK THE BASE METAL OF THE SPECIMEN

A2.1 Repeat the cleaning procedure a number of times. Weigh after each cleaning and plot the mass loss against the total time of cleaning or the number of cleanings, see Fig. A1. The ordinate at

the intersection of the two lines is the mass loss caused by removal of corrosion products alone. The method is particularly applicable to electrolytic cleaning, see Section 4.



FIG. A1 Mass Loss Versus Exposure Time for Specimens During Cleaning.

By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

# Designation: G 4 ~ 68

## Standard Recommended Practice for CONDUCTING PLANT CORROSION TESTS¹

This Standard is issued under the fixed designation G 4; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

#### 1. Scope

1.1 This recommended practice outlines procedures for conducting corrosion tests in plant equipment under operating conditions. It is not intended for atmospheric or underground corrosion tests but may possibly apply to other tests under natural conditions where the procedure has proven satisfactory. Corrosion testing by its very nature precludes complete standardization. This recommended practice, rather than a standardized procedure, is presented as a guide so that some of the pitfalls of such testing may be avoided.

NOTE—The values stated in U.S. customary units are to be regarded as the standard.

#### 2. Interferences

2.1 Tests described herein are probably the best means available for approximating the behavior of metals in service, short of actually constructing and operating a piece of equipment. For best results, certain variables must be considered. These include:

2.1.1 Metal specimens immersed in a specific hot liquid may not corrode at the same rate or in the same manner as in equipment where the metal acts as a heat transfer medium in heating or cooling the liquid. In certain services, the corrosion of heat-exchanger tubes may be quite different than that of the shell or heads. This restriction also applies to specimens exposed in gas streams from which water or other corrodents condense on cool surfaces. Such factors must be considered in both design and interpretation of plant tests.

2.1.2 Effects caused by high velocity, abrasive ingredients, etc. (which may be emphasized in pipe elbows, pumps, etc.), may not be easily reproduced in coupon tests. 2.1.3 The behavior of certain metals and alloys may be profoundly influenced by the presence of dissolved oxygen. It is essential that the test coupons be placed in locations representative of the degree of aeration normally encountered in process.

2.1.4 Corrosion products may have undesirable effects on the product. This possibility is frequently recognized in advance. The extent of possible contamination can be estimated from the loss in weight of the specimen, with proper application of the expected relationships among (1) the area of corroding surface, (2) the mass of the product handled, and (3) the duration of contact of a unit of mass of the product with the corroding surface.

2.1.5 Corrosion products from the plant equipment used in the test may influence the corrosion of one or more of the test metals. For example, when aluminum specimens are exposed in copper equipment, corroding copper will exert an adverse effect on the corrosion of the aluminum. Contrariwise, stainless steel specimens can have their corrosion resistance enhanced by the presence of the oxidizing cupric ions.

2.1.6 The accumulation of corrosion products sometimes can have harmful effects. For example, copper, corroding in intermediate

¹ This recommended practice is under the jurisdiction of the ASTM Commutee G-1 on Corrosion of Metals. This standard is the direct responsibility of Subcommittee G01.12 on In-plant Corrosion Tests.

Current edition effective Sept. 13, 1968. Originally issued as A 224 in 1939. Replaces A 224 – 46. Revised with the aid of Unit Committee T-5A. Corro-

Revised with the aid of Unit Committee T-SA. Corrosion in Chemical Processes, National Association of Corrosion Engineers and ASTM Committee A-10 on Iron-Chromium, Iron-Chromium-Nickel and Related Alloys which formerly held jurisdiction over ASTM Recommended Practice A 224.

strengths of sulfuric acid will have its corrosion rate increased as the cupric ion accumulates. Phenomena such as this will not be recognized from coupon tests in the plant, and must be anticipated from general knowledge and experience, or studied under controlled (laboratory) conditions.

2.1.7 Coupon corrosion testing is predominantly designed to investigate general corrosion. There are a number of other special types of corrosion phenomena of which one must be aware in the design and interpretation of coupon tests.

2.1.7.1 Galvanic corrosion may be investigated by special devices that couple one coupon to another in electrical contact, as for example, by substituting a spacer made from the more noble metal of the couple in place of an insulating spacer. The behavior of the specimens in this galvanic couple are compared with that of insulated specimens exposed on the same holder and the galvanic effects noted. It should be observed, however, that galvanic corrosion can be greatly affected by the area ratios of the respective metals. The coupling of corrosion coupons then yields only qualitative results, as a particular coupon reflects only the relationship between those two metals at the particular area ratio involved.

2.1.7.2 Crevice or concentration cell corrosion may occur where the metal surface is partially blocked from the corroding liquid, as under a spacer. At times it is desirable to know whether a given metal is subject to crevice corrosion in a given environment, whereas in other cases the spacers can be designed to minimize this effect (see below). An accumulation of debris or corrosion products between the coupons can produce misleading results in either accelerating corrosion or protecting the coupons from corrosion.

2.1.7.3 Selective corrosion at the grain boundaries (for example, intergranular corrosion of sensitized austenitic stainless steels) will not be readily observable in weight loss measurements and often requires microscopical examination of the coupons after exposure.

2.1.7.4 Metasomatic corrosion is a condition in which one constituent is selectively removed from an alloy, as in the dezincification of brass or the graphitization of cast iron. Close attention and a more sophisticated eval-

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uation than a simple weight loss measurement is required to detect this phenomenon.

2.1.7.5 Certain metals and alloys are subject to a highly localized type of attack called pitting corrosion. This cannot be evaluated by weight loss. The reporting of nonuniform corrosion is discussed below. It should be appreciated that pitting is a statistical phenomenon and the incidence of pitting can be directly related to the area of metal exposed. For example, a small coupon is not as prone to exhibit pitting as a large one, and it is possible to miss the phenomenon allogether in the AISI Type 300 series stainless steels in chloride-contaminated environments.

2.1.7.6 All metals and alloys are subject to stress-corrosion cracking under some circumstances. This cracking attack occurs under conditions of tensile stress and it may or may not be visible to the naked eye or upon casual inspection. A metallographic examination will confirm this mechanism of attack. It is imperative to note that this usually occurs with no significant loss in weight of the test coupon, although certain refractory metals are an exception to these observations.

#### 3. Apparatus for Mounting Specimens

3.1 Although it is possible to expose specimens to corrosive environments in operating equipment by attaching them to pieces of string, wire, glass, etc., this is usually inadequate. In general, the method of support should be such as to satisfy the following requirements:

3.1.1 Prevent loss of specimens from causes other than corrosion,

3.1.2 Eliminate the possibility of galvanic effects resulting from metal-to-metal contact between specimens or between the vessel and the specimen exposed therein,

3.1.3 Hold specimens firmly in place, and

3.1.4 Provide for protection of specimens against mechanical damage.

3.2 While it is possible to clamp a specimen near its edge, it is not easy to design a clamping arrangement that will provide the necessary electrical insulation without either completely or partially shielding a fairly large area of the specimen from free contact with the corroding solution. A better arrangement is to drill a hole in the specimen and allow the supporting device to pass through the hole. A satisfactory location for the supporting hole is at the center of the specimen so that it cannot be lost from the holder unless either the specimen or the holder is destroyed by corrosion.

3.3 To ensure effective electrical insulation, it is necessary to provide some insulating material between the specimen and the metallic support. This can be accomplished most conveniently by using a tube of some insulating material that will fit over the metal rod. Polyethylene, poly(vinyl chloride), saran, bakelite, ceramics, or fluorinated plastics are satisfactory. The hole in the specimen should be made large enough so that the specimen will slide over the insulating tube. More than one specimen may be exposed on the same holder by insulating or separating the specimens from each other by means of short tubes of insulating material that can be slipped over the insulating tube on the supporting rod. The short tube spacers should be large enough in outside diameter to provide firm support for the specimens without covering more than a small percentage of the total surface. The spacing of the specimens in this arrangement is determined by the length of the insulating spacer. Any insulating material that will withstand the action of the corroding solution may be used. A preferable means of support is the use of individual insulating spacers machined to the desired shape. Figure 1 delineates the dimensions of two types of insulating spacers designed specifically for field corrosion testing. The first type of specimen is designed to minimize concentration cell effects on the face of the specimen. The second type has a sharp shoulder which will tend to lead to crevice corrosion adjacent to the hole in the coupon. The choice between these two types of spacers will lie with the corrosion engineer, based on the type of information he requires.

3.4 Although there are many ways of supporting corrosion coupons in plant apparatus, the following basic types of field corrosion racks are described in some detail as a guide:

3.4.1 A spool rack may be assembled by threading the ends of a supporting rod, and providing end disks or bearing plates against which nuts on the ends of the rod may be turned so as to press the specimens and spacers close together. Two nuts should be used at each end of the rod, the second nut

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acting as a lock nut (Fig. 2). The end plates used as bearing plates should be made larger than the specimens so that they will act as bumpers to keep the specimens from touching any flat surfaces with which the holder may come in contact. The end plates need not necessarily be made of insulating material. Additional metal rods may be used to connect the end plates at points where they will clear the specimens and can be tightened so as to provide additional reinforcement and rigidity to the entire assembly. The rods also protect the specimens from mechanical injury. Support and bracing rods from  $\frac{1}{4}$  in. (6.35 mm) to  $\frac{3}{8}$ in. (9.53 mm) have been found suitable. All metal rods used in the assembly should be made of material which is sufficiently corrosion resistant to ensure the assembly remaining intact for the duration of the test. Stainless steel, Monel Alloy 400, or other suitable nonferrous metals are commonly employed. Individual spacers (Fig. 1) may be used, or a separate insulating tube with insulating washers may be employed. All three modes of mounting coupons are illustrated in Fig. 2. Because these spool type racks have the disadvantage of requiring that the equipment not only be out of service but also be gas-free or otherwise made suitable for entry, other types of field corrosion racks (which are preferably in petrochemical process equipment) have been devised.

3.4.2 The insert rack is fabricated by welding suitable rod or strip to a welding disk that can be held within the bolt circle and flange face of a flange in an unused nozzle. A 1.5 to 2-in. (38.1 to 50.8-mm) nozzle is usually convenient for this installation (Fig. 3). Such racks employ a stout member immediately adjacent to the welding disk, for example, 0.375-in. (9.53-mm) Type 316 stainless steel rod with an 0.25-in. (6.35-mm) rod extension that carries the specimens and spacers. Such racks should also be assembled with a lock nut arrangement. Occasionally, racks of this type may be required for nozzles which are not "blind" but are employed for the fastening of piping to the equipment in question. In such cases the disk can be perforated, and the specimens mounted sidewise on the rack, if required, as indicated in Fig. 3.

3.4.3 For larger diameter pipes or nozzles, a "dutchman" type rack may be employed.

Such a rack will consist of a suitable spool piece with the specimens mounted crosswise on a bar as shown in Fig. 4. Both insert and dutchman corrosion racks require that the equipment be out of service, but they may be installed and removed without extraordinary

precautions in gas freeing the equipment. 3.4.4 The "slip-in" corrosion rack is ideally suited for effecting the entry and removal of corrosion coupons from operating equipment that is in active service. The slip-in rack requires an unused nozzle of suitable size (usually nominal  $1^{1/2}$ -in. pipe size or greater) and a gate valve. The corrosion rack is then assembled from a short length of pipe or tubing with a suitable flange and a packing-gland arrangement made from the bonnet of a  $\frac{1}{2}$ -in. (12.7 mm) stainless steel or suitable alloy valve. An alloy rod of appropriate length is used as the specimen mount as shown in Fig. 5. In the "Out" position the specimens are mounted on the rod and drawn into the recessed area provided by the pipe or tube section. When this is bolted to the gate valve and the valve is opened, the assembly of corrosion coupons may be slid into the operating equipment for exposure. When it is desired to remove the specimens, they are withdrawn into the recessed area, the gate valve is closed, and the entire assembly is then physically removed from the operating equipment.

3.4.5 The design of corrosion racks for plant tests is limited only by the imagination and ingenuity of the corrosion engineer. In specific circumstances, for example, it is possible to convert thermowells into corrosion racks by welding a short extension rod on them. Similarly, racks may be designed to clamp onto agitators, thermowells, or other parts of operating equipment.

3.4.6 When the choice of materials of construction has been narrowed to one or two, it may be desirable to investigate heat-transfer effects with a simple bayonet heater of the design shown in Fig. 6. Either a heating or cooling medium is circulated through the tube side of this testing apparatus, and the effect of the hot or cold wall upon corrosion is observed by visual observation, pit depth measurements, micrometer measurements, etc.

#### 4. Test Specimens

4.1 The size and shape of test specimens is

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influenced by several factors and cannot be rigidly defined. In general, the ratio of surface area to mass should be large so as to favor maximum amount of corrosion loss. This can be accomplished by the use of thin sections. Sufficient thickness, however, should be employed to minimize the possibility of perforation of the specimen during the test exposure. The size of the specimen should be as large as can be conveniently handled, the limitation being imposed primarily by the maximum weight (200 g) that can be handled by an analytical balance and, secondarily, by the problem of effecting entry into operating equipment.

4.2 A convenient size for standard corrosion coupons is 1.5 in. (38.1 mm) in diameter and 0.125 in. (3.18 mm) in thickness with a 0.438-in. (11.1-mm) hole in the center of the round coupon. This size was arrived at as being the maximum size that could easily effect entry through a nominal 1¹/₂-in. nozzle. However, it is also convenient for larger size nozzle entries as well as for laboratory corrosion testing. A convenient standard coupon for spool-type racks is the 2 by 2 by 0.125 in. (50.8 by 50.8 by 3.18 mm) square, if only a few coupons need be made. A round coupon of 2.11 in. (53.5 mm) by 0.125 in. (3.18 mm), or 2.18 in. (55.5 mm) by 0.062 in. (1.59 mm), is sometimes employed. These last measure 0.500 dm² in area.

4.3 Other sizes, shapes, and thicknesses of specimens can be used for special purposes or to comply with the design of a special type of corrosion rack. When the choice of material has been reduced to a few in number in preliminary tests, special coupons should be employed to consider the effect of such factors of equipment construction and assembly as heat treatment, welding, soldering, and cold working or other mechanical stressing.

#### 5. Preparation of Test Specimens

5.1 The edges of test specimens should be so prepared as to eliminate all cold-worked metal except that introduced by stamping for identification. Shearing will, in some cases, cause considerable attack; and, therefore, specimens having sheared edges should not be used. The edges should be finished by machining or polishing. The slight amount of cold working resulting from machining will not introduce any serious error.

5.2 Usually no specific finish is of interest except in the sense that uniformity is desirable when comparing data from different tests. Furthermore, it may be necessary to remove dirt or heat-treating scale from the metal surface. It has been found convenient to standardize on a 120-grit surface in most cases. A surface roughness greater than 120 grit should not be used.

5.3 After the test specimens are cut to size, they should be freed from water breaks by suitable cleaning. In isolated cases, it is desirable to expose specimens with a special surface treatment. For example, in some applications, stainless steels may be prepassivated by a 30-min immersion in 10 to 20 percent nitric acid at 60 C. In most cases, however, special pretreatments are unnecessary and undesirable.

5.4 The weight of each specimen should be determined to the nearest 0.1 mg on an analytical balance.

#### 6. Number of Test Specimens

6.1 For statistical validity, it is desirable to expose replicate specimens. When corrosion tests are performed in the laboratory under standard conditions, duplicate specimens will suffice for an accuracy of  $\pm 10$  percent. However, this reflects the reproducibility of certain standardized tests, and does not necessarily hold true for plant corrosion testing. It is possible, although not probable, to have rather widely different results on replicate specimens exposed on the same rack in a given test.

6.2 In multiple exposures, it is probable that there will be considerable variation in the results from one exposure to the other because of changes in operating conditions. Under such circumstances an evaluation should be based on the statistics of a limited number of observations.²

6.3 For a limited number of observations (for example, ten or less) the range w between maximum and minimum values provides more definitive values than does the standard deviation. In practice, it is usually desired to establish a "confidence interval", that is, the distance on either side of the average in which one would expect to find the true value 95 percent of the time. This is established by multiplying the range w by a factor t. The 95

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percent confidence interval factors t are as follows:

n	1
2	6.4
3	1.3
4	0.72
5	0.51
Confidence inte	$rval = \bar{x} \pm tw$

where:

x = average of *n* observations,

w = range, and

$$t = factor.$$

For example, if four successive tests give corrosion rates of 15, 20, 25, and 20 mils/year, the average  $(\bar{x})$  is 20, and the range is 25 - 15 = 10. Then the 95 percent confidence interval is  $20 \pm 10 (0.72)$  or  $20 \pm 7.2$  mils/year (1 mil/year = 0.0254 mm/year). A special consideration can also be applied to evaluate whether a doubtful observation should be disregarded. This is discussed in detail in the referenced article.

#### 7. Identification of Test Specimens

7.1 For purposes of identification, a record should always be made of the relative positions of the test specimens on the holder. If identification marks are obliterated by corrosion, careful handling of the specimens is required to maintain identity.

7.2 Although it may be necessary in special instances to notch the edge of the specimens for identification, it is preferable that they be stamped with a code number. The stamped number has an additional advantage in that, should a specimen show a preferential attack at the stamped area, a warning is given that the material is susceptible to corrosion when cold worked. It is also possible in some instances to detect stress-corrosion cracking emanating from the stamped areas. With such indications, the investigator is forewarned and can reject the material from further consideration or may study further the effects of cold working or stress upon the corrosion behavior. Note, however, that although the presence of such localized attack is a positive indication, absence of attack is not a guarantee of immunity from attack in operating equipment.

² Dean, R. B., and Dixon, W. J., "Sîmplified Statistics for Small Numbers of Observations," *Analytical Chemistry*, ANCHA, Vol 23, No. 4, April, 1951, pp. 636-638.

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#### 8. Installation of Specimen Holder

8.1 The location of the test specimens in the operating equipment will be governed by the information that is desired. This may require tests at more than one location in the same piece of equipment, such as below the level of the test liquid, at the level of the liquid, or in the vapor phase.

8.2 It is desirable to have the specimen holder securely fixed in place. The preferred position of the holder is with the long axis horizontal so as to prevent drippage of corrosion products from one specimen to another. Preferably, the holder should be so placed that any flow of liquid will be against the edges of the specimens. The same condition of agitation of the liquid should then be encountered by all specimens.

#### 9. Duration of Exposure

9.1 The duration of exposure may be based on known rates of deterioration of the materials in use. More often, it is governed by the convenience with which plant operations may be interrupted to introduce and remove test specimens. In many tests, some materials may show little or no attack while other materials may be completely destroyed. In general, the duration of the test should be as long as possible commensurate with the resistance of the materials under test. In special cases, the duration may be established in regard to some specific phase of the operation, as for example to study corrosion in one step of a batch process. Possible changes in the rate of corrosion may be studied either by successive exposures or by the installation of several sets of specimens at the same time, which can be removed one set at a time at different intervals. The minimum duration is commonly defined by the equation:

Minimum hours of test = 2000/mils/year.

#### 10. Removal of Specimens from Test

10.1 The condition and appearance of the holder and specimens after removal from equipment should be noted and recorded. Specimens should then be carefully washed, either in water or in a suitable solvent, to remove all soluble materials from the surface of the specimens. In removing the specimens from the holder, care should be taken to keep them in proper sequence relative to each other so that any specimen may be identified from the original record of its position on the holder. This is important if corrosion has been so severe that identification marks have been removed.

10.2 A record should be made of the appearance and adhesion of any coatings or films on the surface of the specimens after washing. It may be desirable to photograph the specimens. Color photographs may be of value. Samples of any products or films resulting from corrosion may be preserved for future study.

#### 11. Cleaning³ and Weighing Test Specimens

1.1 The surfaces of the test specimens should be thoroughly cleaned of all corrosion products. Removal of corrosion products from the specimens may not be a simple procedure. No hard and fast rules can be laid down since the cleaning procedure adopted will depend on the base material as well as the nature of the corrosion products. It will be necessary for the investigator to study the problem and decide upon the most suitable procedure.

11.2 It is essential that the base metal be unattacked either by the cleaning reagent or by compounds formed by reaction between the cleaning reagent and corrosion products or other deposits on the specimen. A preliminary solvent cleaning may be necessary to remove organic deposits. The simplest cleaning procedure is to scrub the specimens with a flat fiber brush using a mild abrasive soap. Care must be taken that no base metal is removed by abrasion. Acid or alkaline solutions of suitable nature and strength may be employed, contingent upon their being noncorrosive to the base metal. For example, a copper flash on stainless steel or Hastelloy Alloy C can be safely removed in concentrated nitric acid. On the other hand, a copper flash on Monel Alloy 400 or Hastelloy Alloy B should be removed with a mixture of peroxide and ammonium hydroxide which will not significantly attack the base metal. A solution of 5 percent stannous chloride and 2 percent antimonious chloride in concentrated hydrochloric acid may be used to remove rust deposits from steel. This

³ ASTM Recommended Practice G 1, for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, which appears in *Annual Book of ASTM Standards*, Part 31.

solution has an added advantage in that the final disappearance of the last vestige of ferric oxide is readily apparent to the naked eye. For iron, steel, and alloy steels, a hot caustic solution (20 percent) with 200 g of zinc dust added per liter is effective for loosening deposits which can then be scrubbed off.

11.3 A cleaning method used by many investigators for a variety of materials consists in making the specimen the cathode in a hot dilute sulfuric acid solution under the following conditions:

11.3.1 Solution-5 weight percent of sulfuric acid plus 2 ml of an appropriate commercial inhibitor per liter of solution.

11.3.2 Anode Carbon-cathode-test specimen.

11.3.3 Cathode Current Density-20 A/ dm².

11.3.4 Temperature-165 F (73.9 C).

11.3.5 Exposure Period-3 min.

11.4 Another method which is sometimes effective for removal of iron oxides is immersion of the specimen in a hot solution of ammonium acetate.

11.5 After cleaning, the weight of each specimen should be determined to the nearest 0.1 mg on an analytical balance and the loss in weight calculated. The corrosion rate in mpy (mils per year) can be calculated using the following equation:

 $mpy = \frac{\text{weight loss, g \times 534,000}}{\text{metal density, g/cm^3 \times metal area, in.}^2} \times \text{hours exposure}$ 

The corrosion rate may be translated into other terms as discussed below.

#### 12. Examination of Specimen Surface

12.1 The specimen should be carefully examined for type and uniformity of surface attack such as etching, pitting, metasomatic attack, tarnish, film, scale, etc. If pitting is observed, the number, size and distribution, as well as the general shape and uniformity of the pits should be noted. The maximum and minimum depth of the pits can be measured with a calibrated microscope or by the use of a depth gage. Photographs of the cleaned specimens will serve as an excellent record of the surface appearance.

12.2 A distinction should be made between pits occurring under the insulating spacers

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and those occurring on the boldly exposed surface. As previously noted, pitting at or under the insulating spacers is an indication of the susceptibility of the material to "concentration cell" effects, whereas pitting on the surface is indicative of the intrinsic pitting tendency of the environment.

12.3 In the case of severe pitting of the specimen, the weight loss is of little value and the study of the number, size, and distribution of the pits will be of much more importance. Sometimes a pit-type of corrosion is initiated but is self-healing and stops. A more detailed study of pitting is necessary before a definite conclusion can be reached as to the desirability of rejecting a material because it has a tendency to pit.

12.4 If an alloy is known to be susceptible to localized corrosion on a microscale, such as the phenomenon of intergranular corrosion in stainless steel, dezincification in brass, or stress corrosion cracking of any kind, the specimen should be bent after the previously outlined examination is completed, and any cracks which develop on the surface noted. The results should be compared with those obtained on similar bend tests on unexposed specimens from the same lot of material.

12.5 Microscopical examination of the surface and interior of the specimens may be made if deemed necessary. A low power shoptype binocular microscope is ideal for many of these examinations, although a metallographic examination may be needed.

12.6 The behavior of the metals in galvanic couples can be compared with that of insulated specimens exposed at the same time, and any galvanic effects, including cathodic protection, can be observed. As mentioned earlier, such tests are only qualitative as the magnitude of the galvanic effect will be influenced by the relative areas of the two metals comprising the couple. The results will apply directly only to assemblies where the ratio of areas used in making the tests is similar to the ratio of areas anticipated in the fabricated assembly.

#### 13. Report

13.1 In reporting results of corrosion tests, the conditions of the test should be described in complete detail with special attention being given to the following: 13.1.1 Corrosive media and concentration,

13.1.2 Type of equipment in which the test was made,

13.1.3 Process carried out in the operating equipment,

13.1.4 Location of specimens in the operating equipment,

13.1.5 Temperature of corrosive media (maximum, minimum, and average),

13.1.6 Oxidizing or reducing nature of corrosive media,

13.1.7 Amount and nature of aeration and agitation of corrosive media,

13.1.8 Duration and type of test (if equipment was operated intermittently during the tests, the actual hours of operation should be stated as well as the total time of the test),

13.1.9 Surface condition of specimen (polished, machined, pickled, 120 grit, etc.), and

13.1.10 Units for expressing corrosion loss. The unit for expressing corrosion rate should be mils penetration per year in cases where the corrosion has been substantially uniform in distribution over the surface of the specimen. If this figure is representative, it may be correlated with the thickness of the equipment in the evaluation of the probable life. It is possible to convert this penetration unit into other terms such as millimeters per year or milligrams per square decimeter per day for comparison with other data.⁴ Any such expression will be subject to error to the extent to which nonuniform distribution of corrosion and changes of corrosion rates with time occur. In connection with the latter, it is often desirable to carry out the testing procedures so as to provide data from which curves can be plotted to illustrate changes in corrosion rates with time.

13.2 The depth of pits should be reported in 0.001 in. (0.02 mm) for the test period and not interpolated or extrapolated to thousandths of an inch per year or any other arbitrary period. The size, shape and distribution of the pits should be noted.

#### 14. Supplementary Tests

14.1 Supplementary laboratory tests should always be made when it is desired to study the effect of one or more of the variables encountered in plant tests. They are particularly desirable if there is any reason to believe that the products of corrosion, or the metal used for the equipment in which the test was conducted, might have had a controlling influence on the behavior of any metal in which there is further interest.

14.2 Special supplementary field tests should be made if there is any reason to believe that stress corrosion cracking, intergranular corrosion, or any other special metallurgical phenomena may be anticipated.

⁴See Appendix A2 of ASTM Method A 279, Total Immersion Corrosion Test of Stainless Steels, which appears in the *Annual Book of ASTM Standards*, Part 3.





FIG. 1 Tubular Plastic Spacers.



FIG. 2 Spool Rack.





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FIG. 4 Dutchman Racks.





FIG. 6 Hot-Wall Tester.

By publication of this standard no position is taken with respect to the validity of any patent rights in connection therewith, and the American Society for Testing and Materials does not undertake to insure anyone utilizing the standard against liability for infringement of any Letters Patent nor assume any such liability.

# Designation: G 15 - 71

### Standard Definitions of Terms Relating to CORROSION AND CORROSION TESTING¹

This Standard is issued under the fixed designation G 15; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval.

anode—the electrode of an electrolytic cell at which oxidation is the principal reaction. (Electrons flow away from the anode in the external circuit. It is usually the electrode where corrosion occurs and metal ions enter solution.)

anion—a negatively charged ion.

- **cathode**—the electrode of an electrolytic cell at which reduction is the principal reaction. (Electrons flow toward the cathode in the external circuit.)
- cathodic corrosion—corrosion of a metal when it is a cathode. It usually happens to amphoteric metals as a result of a rise in pH at the cathode or as a result of the formation of hydrides.

**cation**—a positively charged ion.

- **concentration cell**—an electrolytic cell, the emf of which is caused by a difference in concentration of some component in the electrolyte. This difference leads to the formation of discrete cathode and anode regions.
- **corrosion potential**—the potential of a corroding surface in an electrolyte relative to a reference electrode measured under opencircuit conditions.
- electrolytic cleaning—a process of removing soil, scale, or corrosion products from a metal surface by subjecting it as an electrode to an electric current in an electrolytic bath.
- equilibrium (reversible) potential—the potential of an electrode in an electrolytic solution when the forward rate of a given reaction is exactly equal to the reverse rate. The equilibrium potential can only be defined with respect to a specific electrochemical reaction.

- galvanostatic—pertaining to an experimental technique whereby an electrode is maintained at constant current in an electrolyte.
- inhibitor—a chemical substance or combination of substances, which when present in the proper concentration and forms in the environment, prevents or reduces corrosion.
- **long-line current**—current which flows through the earth from an anodic to a cathodic area of a continuous metallic structure. Usually used only where the areas are separated by considerable distance and where the current results from concentration-cell action.

metallizing-See thermal spraying.

- **open-circuit potential**—the potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from it.
- overvoltage—the change in potential of an electrode from its equilibrium or steady state value when current is applied.
- passivator—a type of inhibitor which appreciably changes the potential of a metal to a more noble (positive) value.
- **potentiostat**—an instrument for automatically maintaining an electrode at a constant potential or controlled potentials with respect to a suitable reference electrode.
- redox potential the potential of a reversible oxidation-reduction electrode measured with respect to a reference electorde, corrected to the hydrogen electrode, in a given electrolyte.

stress-corrosion cracking-a cracking process

¹ These definitions are under the jurisdiction of Committee G-1 on Corrosion of Metals and are the direct responsibility of Subcommittee II on Nomenclature. Effective Jan. 8, 1971.

requiring the simultaneous action of a corrodent and sustained tensile stress. This excludes corrosion-reduced sections which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion which can disintegrate an alloy without either applied or residual stress.

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thermal spraying—a group of processes wherein finely divided metallic or nonmetallic materials are deposited in a molten or semimolten condition to form a coating. The coating material may be in the form of powder, ceramic rod, wire, or molten materials.

# Designation: G 16 - 71

## Standard Recommended Practice for APPLYING STATISTICS TO ANALYSIS OF CORROSION DATA¹

This Standard is issued under the fixed designation G 16; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reproval.

#### 1. Scope

1.1 Corrosion scientists and engineers are making increased use of statistical methods. not only in laboratory programs, but often in field failure analysis. Application of statistical methods and interpretation of the results obtained is rendered difficult by the large number of complex techniques that are available and a lack of standardization between analytical methods employed by various groups. Statistics as a discipline applies to nearly all physical, biological, and economic sciences; this has led to development of a large number of methods that are generally applicable and complex. In contrast, the specific application of statistics to corrosion problems often involves simplification and use of a limited number of methods.

1.2 The purpose of this practice is to provide a set of sample procedures that are in current usage in statistical analysis of corrosion experiments. It is recognized that the procedures selected are but a fraction of methods available and that complete agreement on specific methods selected may not be possible. The examples included are intended to provide a method for planning corrosion experiments, analyzing data obtained, and establishing the degree of confidence that can be placed in the results of specific experimental or field applications data. Alternative methods or improved approaches are constantly being developed that may provide more complete analysis and understanding of specific experiments. Accordingly, Subcommittee G01.03 would welcome the comments and criticisms of readers so that future revisions of the procedure may be updated to reflect statistical methods that are most relevant to analysis of corrosion experiments.

1.3 The recommended practice includes the following sections:

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## 2. Errors, Their Recognition, and Treatment (1)²

2.1 Engineers are frequently faced with the problem of making measurements in the laboratory or in the field that are not completely accurate. It is common practice to repeat a set of measurements; this repetition allows application of statistics to determine the degree of precision obtained. The basis for this approach is that random errors tend to cancel out when a large number of measurements are averaged. For example, suppose that a technician has been asked to prepare a large number of nominally ¹/₈-in. thick corrosion samples by cutting them from a large diameter bar of a relatively soft alloy. If the cutting is judged by

¹ This recommended practice is under the jurisdiction of ASTM Committee G-1 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.03 on Statistical Analysis and Planning of Corrosion.

Effective Jan. 8, 1971.

² The boldface numbers in parentheses refer to the list of references at the end of this recommended practice.

eye, it is obvious that not all of the samples will be the same thickness. However, when all the samples are measured and an average thickness is calculated, it will be found that most values lie close to the numerical average or mean.

2.2 Statistical methods cannot eliminate experimental error, but statistics can provide an indication of the magnitude of the possible errors. Statistical methods are particularly useful in establishing the degree of confidence that can be placed in a given measurement or in a value calculated from a measurement. Statistical analysis is based on the premise that errors follow a normal distribution pattern or some special case. The types of errors that occur in experiments arise in measurements or in handling of data. Proper care during the experiment and in subsequent calculations is essential to minimize unnecessary errors and to ensure that all sources of error can be properly identified and calculated.

2.2.1 Normal Distribution-In the example above if the number of samples of each measured thickness is plotted against the thickness, a curve called a histogram will be obtained. Frequently this curve will approximate the shape shown in Fig. 1. This is the so-called normal distribution curve. It has certain characteristics. It can be divided into equal-size segments on either side of the mid point which will include a certain fixed percentage of all measurements. The first two are located equal distances from the mid point on either side to include 68.27 percent of the measurements. These represent one standard deviation  $(\pm \sigma)$ ; the standard deviation is discussed in the next section. Two standard deviations  $(\pm 2\sigma)$  on the abcissa will then encompass 95.45 percent of the measurements and three standard deviations  $(\pm 3\sigma)$  will encompass 99.73 percent of the measurements. It should be noted that not all experimental error is normally distributed, and it is a good idea to plot histograms to determine if the data fit a normal distribution. This is only possible when a large number of points are available, for example, 20 or more.

2.2.2 Systematic Error—In the example above suppose 10 people measured the thickness of each of the corrosion coupons. The plots of the resulting data for each person would generally also produce a normal distri-

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bution curve. However, the results for those who pressed down hard with their micrometers on the soft metal would produce a low average and a curve whose maximum was located to the left of that shown in Fig. 1. Those who did not press down firmly would obtain a high average and a curve to the right of that shown. This type of error is a function of the experimental technique and is not a random error. It is called bias and is a systematic error which cannot be handled by statistical analysis alone, although statistical methods can sometimes be used to detect and identify bias.

2.2.3 Mistakes—Mistakes either in carrying out an experiment or in calculations are not a characteristic of the population and can preclude statistical treatment of data, or lead to erroneous conclusions if included in the analysis. Sometimes mistakes can be identified by statistical methods by recognizing that the probability of obtaining a particular result is very low.

2.2.4 Significant Figures:

2.2.4.1 Care should be exercised in reporting results to show the proper number of significant figures. The location of the decimal point can be used for this purpose. For example the number 2700 can be written as  $2.7 \times 10^2$  to show two significant digits, that is, an indicated accuracy of  $\pm 100$ . On the other hand 2700, indicates an accuracy of  $\pm 1$ .

2.2.4.2 In carrying out calculations it is good practice to retain one insignificant digit through the calculation to minimize rounding off errors. This insignificant digit should be rounded off in the result. For example the sum of 2700. + 7.07 should be reported as 2707. not 2707.07.

2.2.5 Propagation of Error in Calculation:

2.2.5.1 Mathematical operations with experimental data will cause errors in the data to change in predictable ways. Two types of errors are frequently discussed: maximum error and probable error. Estimates of maximum error can usually be found in descriptions of instruments, etc., and generally include systematic as well as random error. Probable error refers to the standard deviation due to random error in systems where it is known or assumed that bias is negligible.

2.2.5.2 Maximum error calculations can be
handled by equation:

$$\Delta Q = \Sigma_{i=1}^{n} + \partial Q / \partial X_i + \Delta X_i \tag{1}$$

where

= calculated quantity of interest, a func-Q tion of *n* measured variables denoted  $X_i$ ,

 $\Delta Q$  = maximum error in Q, and

 $\Delta X_i$  = maximum error in the independent variables.

This expression assumes that all of the X's are independent variables. If this is not true then all partial deviations with dependent variables must be grouped by independent variables inside the absolute value bracket and the sign of the partial deviations considered in each group.

2.2.5.3 If standard deviation information is available then a different equation should be used, namely:

$$\sigma(Q) = [\sum_{i=1}^{n} (\partial Q / \partial X_i)^2 \sigma^2(X_i)]^{1/2}$$
(2)

where  $\sigma(X)$  represents the standard deviation of X and all the other terms are defined above.

2.2.5.4 Again we assume that all X's are independent of one another. Both Eqs 1 and 2 can be simplified in specific cases. For example if

$$Q(X_1 X_2 X_3 \cdots X_n) = A(X_1)^a (X_2)^b \cdots (X_n)^j \quad (3)$$

then Eq 1 can be simplified to:

$$\Delta Q/Q = a(\Delta X_1/X_1) + b(\Delta X_2/X_2) + \cdots + j(\Delta X_n/X_n) \quad (4)$$

and with simple product functions the percent errors are additive. Another simplification occurs in the case when:

$$Q = aX_1 + bX_2 + \cdots jX_n$$

Then Eq 1 becomes:

$$\Delta Q = a\Delta X_1 + b\Delta X_2 + \ldots + j\Delta X_n \tag{5}$$

2.2.5.5 For an application of these calculations, consider the errors introduced into the results from limited precision of equipment such as a balance. Weighing is a common measurement in conducting corrosion tests. The difference between initial and final weights is often used to calculate corrosion rates. These weighings are usually conducted on a conventional laboratory analytical balance that is accurate to  $\pm 0.2$  mg. In weight loss, L equals the initial weight minus the final

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weight. From Eq 5 the maximum error between the initial and final weights of a corroded specimen is 0.4 mg. If the observed difference in weight is only 1 mg, the maximum possible error is  $(0.4/1) \times 100 = 40$  percent. If the difference is 10 mg, the error is only 4 nercent.

2.2.5.6 For another example, the velocity of flowing water is to be measured in a corrosion test. The water will be bypassed into a container for a given period of time and the amount collected will be weighed. Knowing the pipe diameter, the average velocity can then be calculated from the following equation:

$$V_{\rm avg} = W/tA\rho = 4W/\pi D^2 t\rho \tag{6}$$

where:

- W = weight of water,
- A = cross-sectional area,
- D = diameter,
- t = time, and
- = density. ρ
- $\Delta W = \pm 5$  lb—An old scale will be used which is accurate to  $\pm 5$  lb. About 100 Ib will be collected.
- $\Delta t = \pm 1$  s—Accuracy of watch and observer is estimated to be  $\pm 1$  s. Total time will be about 70 s.
- $\Delta D = \pm 0.03$  in.—Out-of-roundness and caliper errors are expected to be ±0.03 in. for 1-in. diameter pipe (inside diameter).
- ±0.02 lb/ft³-Temperature measure- $\Delta \rho =$ ment is expected to be  $60 \pm 3$  F, which corresponds to densities limits of 62.38 and 62.34 lb/ft³. Thus, the error is of the order of 0.1 percent. This is an order of magnitude less than the other errors and thus the error in this term can be neglected.

The maximum error then can be calculated by Eq 1.

$$\Delta V = \left| \frac{4}{t\pi D^2 \rho} \Delta W \right| + \left| \frac{4W}{\pi D^2 \rho t^2} \Delta t \right| + \left| \frac{8W}{t\pi \rho D^3} \Delta D \right|$$
$$= \frac{4 \times 144}{70 \times 3.14 \times 1 \times 62.3} \Delta W$$
$$+ \frac{4 \times 100 \times 144}{3.14 \times 1 \times 62.3 \times (70)^2} \Delta t$$
$$+ \frac{8 \times 100 \times 1728}{70 \times 3.14 \times 62.3 \times 1} \Delta D$$

ASID.

 $= 0.042 \Delta W + 0.060 \Delta t + 100 \Delta D$ = 0.52 ft/s  $V_{avg} = 4W/\pi D^2 t \rho$ =  $\frac{4 \times 100 \times 144}{3.14 \times 1 \times 70 \times 62.3}$ = 4.2 ft/s

Percent error =  $(0.522/4.21) \times 100 = 12$  percent

2.2.5.7 A simplified form of Eq 1 can be used in this case because Eq 6 is of the form shown in Eq 3. Rewriting Eq 4 for this case we have:

$$\Delta V/V = 1 \Delta W/W + 1 2\Delta D/D + 1 \Delta T/T$$

Then by inspection:

 $\Delta V/V = (5/100) + (2 (0.03)/1) + (1/70)$ = 0.124 = 12.4 percent

and

$$\Delta V = 0.124 \times 4.21 = 0.52 \, \text{ft/s}$$

2.2.5.8 Another advantage to this simplification is that it is dimensionless and so eliminates the need for converting units. Note in the example given D is measured in inches but must be converted to feet to be used in the equation given. Also note that the greatest reduction in error can be made by increasing the accuracy of weighing and of measuring the pipe diameter.

2.2.5.9 Simplification of Eq 2 along the lines shown above are also possible. For example in the above case if the error figures were standard deviation rather than maximum errors the result would become:

 $\sigma(V)/V = [(0.05)^2 + (2)^2 \cdot (0.03)^2 + (1/70)^2]^{1/2}$ = [0.0063]^{1/2} = 0.0795 or 8.0 percent

Then the standard deviation of V would be 0.34 ft/s.

#### 3. Standard Deviation (2)

3.1 The 24 values listed under x in Table 1 are weight loss data in mg/dm²-day for a particular alloy exposed several months to sea water. An over-all description of data may be expressed as (1) the mean,  $\bar{x}$ , the sum of all values divided by the total number of values, n; (2) the median, the mid value (the average of the 12th and 13th values since n is even) in ascending order; often more meaningful than the mean when there are one or two values vastly different from the rest, and (3) the standard deviation,  $\sigma$ .

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3.2 The standard deviation of a large group of numbers is defined below

$$\sigma = \sqrt{\Sigma d^2/n} \tag{7}$$

 $\sigma$  = standard deviation,

- $d = x \bar{x}$  (where x = value and  $\bar{x} =$  the mean), and
- n = total number of observations.

The definition also holds for a small group of numbers if  $\bar{x}$  is known independently; however, if  $\bar{x}$  is not independently known, then with a limited number of observations, only an estimate of the standard deviation can be made which is:

$$s = \sqrt{\Sigma d^2/(n-1)} \tag{8}$$

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$$s = \sqrt{n\Sigma x^2 - (\Sigma x)^2/n(n-1)}.$$
 (9)

Equation 9 is convenient if a desk calculator is used. The square of the standard deviation,  $\sigma^2$ , is called the variance of the data. The computations have been carried out in Table 1, and the mean and the estimate of the standard deviation are found to be 177.17 and  $\pm 10.71$  mg/dm²-day, respectively.

If data from the 24 samples follow normal distribution (well-known bell-shaped curve), then

- $\bar{x} \pm s$  will include 68.27 percent of the results, on the average
- $\bar{x} \pm 2s$  will include 95.45 percent of the results, on the average
- $\bar{x} \pm 3s$  will include 99.73 percent of the results, on the average.

### 4. Probability Curves (2, 3, 4)

4.1 Arithmetic probability paper is so constructed that data from a normal distribution, when plotted on the paper will be randomly distributed about a straight line. To plot the curve, the data must be arranged in ascending order of value and the cumulative percent of tests must be determined for each observation from the following equation:

$$P(\%) = 100 \left[ (i - 0.375) / (n + 0.25) \right]$$
(10)

where:

- *i* = position of data point in total ranking, and
- n = total number of data points.
- The data from Table 1 are used to calculate P(%)'s which are shown in Table 2.

4.2 The results are plotted on arithmetic probability paper³ in Fig. 2. It is not necessary to fit a straight line to these data since the line can be plotted accurately from the mean and the standard deviation. The mean  $(\vec{x})$ , 177.17, is plotted at 50 percent on the abscissa and the mean plus the standard deviation  $(\vec{x} + s)$ (177.17 + 10.71) is plotted at 84.13 percent on the abscissa. A straight line through these points establishes the slope of the curve. (The mean minus the standard deviation  $(\vec{x} - s)$ could also have been used as one of the points.)

4.3 Some data exhibit log-normal distribution. For example, the time to fracture of aluminum alloys in stress-corrosion cracking tests in salt solution follows such a distribution. A plot of these data on log-normal probability paper produces a straight line. Endurance times for the stress-corrosion cracking of an aluminum alloy and the log-normal probability plot of these data are presented in Table 3 and Fig. 3, respectively (3). The probability curves are plotted from the log mean (at 50 percent) and the log mean minus or plus the standard deviation of the logs (at 16 percent, 84 percent) given in Table 3.

4.4 A special form of distribution is extreme value analysis. This type of distribution has been used to analyze maximum pit depths. The pit depth distribution on a given number of corrosion coupons may follow a normal distribution on each coupon, but the maximum pit depths on each of the coupons follow a special distribution of extreme values. The mathematics of extreme values are complex, but practical use of the technique has been simplified by the use of extreme probability paper.

4.5 Aziz (4) has used extreme probability paper in the study of the pitting of aluminum alloys. As an example, consider the maximum pit depths observed for sets of 9 or 10 samples exposed to tap water for exposure periods ranging from 2 weeks to 1 year presented in Table 4. The data are ranked in order of increasing pit depth. The plotting position for each ranking is determined by R/(n + 1)where R = rank and n = total number of specimens. Thus, where 9 specimens were examined, the plotting position for the first specimen is 1/(9 + 1) = 0.100, for the second is 2/(9 + 1) = 0.200 etc. For 10 specimens

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the plotting position for the first specimen is 1/(10 + 1) = 0.0909 etc.

4.6 The above data when plotted on extreme probability paper produce the straight lines shown in Fig. 4, thus indicating an extreme value distribution. By extrapolating the plotted lines, one can make certain predictions. For example, with the 2-week data it can be seen that the probability of obtaining a pit 760  $\mu$ m in depth or less is 0.999 and that the probability of obtaining a pit greater than 760  $\mu$ m is only one in 1000; whereas the observed deepest pit depth was 580  $\mu$ m.

# 5.1 Curve Fitting—Method of Least Squares (5)

5.1 To fit data to a linear plot of the form y = mx + b, it is necessary to solve two equations:

$$m\Sigma x^{2} + b\Sigma x = \Sigma xy$$
  

$$m\Sigma x + bn = \Sigma y$$
  

$$m = (n\Sigma xy - \Sigma x\Sigma y)/[n\Sigma x^{2} - (\Sigma x)^{2}]$$
  

$$b = (l/n)(\Sigma y - m\Sigma x)$$

where:

or

 $\Sigma x = \text{sum of all } x \text{ points},$ 

 $\Sigma y = \text{sum of all } y \text{ points},$ 

 $\Sigma x^2$  = sum of squares of x points,

- $\Sigma xy =$ sum of x points multiplied by y points, and
- n = number of points.

For a parabola of the form  $y = ax^2 + bx + c$ three equations must be solved:

$$a\Sigma x^{4} + b\Sigma x^{3} + c\Sigma x^{2} = \Sigma x^{2}y$$
  
$$a\Sigma x^{3} + b\Sigma x^{2} + c\Sigma x = \Sigma xy$$
  
$$a\Sigma x^{2} + b\Sigma x + cn = \Sigma y$$

5.2 Data for exposure of five replicate specimens of Zircaloy-2 to 750 F-1500 psi steam are presented in Table 5. It is known that the corrosion kinetics of Zircaloy-2 obey two rate laws, an initial cubic-to-parabolic rate followed by a linear rate. In 750 F steam the rate becomes linear after about 42 days. Thus the data in Table 5 comprise the *initial* reaction kinetics which follows a power formula of the general type:

$$W = kt^a$$

where:

W = weight gain (the oxide is extremely adherent),

 $^{^{\}rm 3}\,\text{Keuffel}$  and Esser No. 359-24 has been found satisfactory.

k = a rate constant,

t = time, and

a = dimensionless.

The above equation can be expressed in the logarithmic form:

 $\log W = a \log t + \log k$ 

A plot of the above logarithms produces a straight line whose slope is *a*. Thus, the logarithms of the data can be used to fit a curve by the least squares method for a straight line by setting:

$$y = \log W$$
  

$$x = \log t$$
  

$$b = \log k$$
  

$$m = a$$

5.3 The logarithmic forms of the data and the required summations are shown in Table 6 (although only one value is given for x there is one for each value of y, that is five for each exposure time). The calculations of m and bare shown below:

$$m = \frac{m\Sigma xy - \Sigma x\Sigma y}{n\Sigma x^2 - (\Sigma \dot{x})^2}$$
  
=  $\frac{30 \times 41.303 - 27.75 \times 39.92}{30 \times 35.001 - (27.75)^2} = 0.469$   
 $b = \frac{1}{n} (\Sigma y - m\Sigma x)$   
=  $\frac{39.92 - (0.469 \times 27.75)}{30} = 0.897$   
 $\log k = b = 0.897$   
 $k = 7.89$ 

a = m = 0.469

Thus, the equation of the curve best fitting the data is

$$W = kt^a$$
  
 $W = 7.89t^{0.469}$ 

5.4 The above curve is plotted on log-log paper in Fig. 5. The curve also shows a plot of the 95 percent (2s) limits of data. These were obtained from the estimate of standard deviation of residuals about the curve, calculated from the equation:

$$s = \sqrt{\Sigma d^2/(n-2)}$$

where  $d = y - \hat{y}$  and  $\hat{y}$  is the weight gain predicted from the above equation at a given level of exposure time *t*. The logarithms of data presented in Table 6 were used on the assumption that variance of logarithms of data is in-

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dependent of means at each exposure period. (Variance should be independent of means of function of the data (arithmetic, logarithms, exponential, etc.)) The difference, d, from the predicted value,  $y - \hat{y}$ , was determined for each exposure period. All the d's were squared and summed and s was determined for the entire sample.

$$s = \sqrt{\Sigma d^2/(n-2)} = \sqrt{0.0644/(30-2)} = 0.048$$

At the 95 percent confidence interval 2s = (2) $(\pm 0.048) = \pm 0.096$ . Then the calculations of the lines for 95 percent confidence are as follows: (For 1- and 42-day exposures).

$$log w = log k + a log t \pm 2s$$
At l day, log w = 0.897 + (0.469 × 0) ± 0.096  
= 0.897 + 0.096 = 0.991  
= 0.897 - 0.096 - 0.803  
At 42 days, log w = 0.897 + (0.469 × 1.62)  
± 0.096  
= 0.897 + 0.760 + 0.096  
= 1.753  
= 0.897 + 0.760 - 0.096  
= 1.561

The antilogs are:

 $\begin{array}{r} \mbox{At I day, 0.991} = 9.79 \mbox{ mg/dm}^2 \\ 0.803 = 6.36 \mbox{ mg/dm}^2. \\ \mbox{At 42 days, 1.753} = 56.6 \mbox{ mg/dm}^2 \\ 1.561 = 36.4 \mbox{ mg/dm}^2 \end{array}$ 

5.5 These deviations do not include the effect of variable slope which becomes increasingly important in regions away from the mean. The variable slope could be plotted in Fig. 5 as two lines passing through the data mean with slopes of  $m \pm 2s$  (m).

### 6.1 Estimate of Limits that Include True Value of Mean (Confidence Limits) (6)

6.1 When dealing with a small number of observations, the estimate of the limits that include the true value of the mean can be obtained from:

$$\Delta = \pm t \left( s / \sqrt{n} \right)$$

where:

s = estimate of standard deviation,

n = number of observations, and

t = student's t from published tables.

For example, the 14-day-75 F steam data for Zircaloy-2 are calculated below:

Five observations: 25.6, 25.5, 24.3, 26.9, and 27.1  $mg/dm^2$ Mean  $(\vec{x}) = 25.9$ 

Estimate of standard deviation  $s = \sqrt{\sum d^2/(n-1)}$ =  $\sqrt{5.29/(5-1)} = 1.15$  🚯 G 16

The values of t are obtained from Table 7 at the appropriate degrees of freedom (n - 1). For 4 degrees of freedom the value of t =0.741 at 0.50 probability, 2.776 at 0.95 probability, and 4.604 at 0.99 probability. Then calculating the limits that would include the true mean at particular levels of confidence:

### $\Delta = \pm t \left( s / \sqrt{n} \right)$

Confidence Limits, percen

, percent	Deviation
50	$\Delta = \pm 0.741 \times (1.15/\sqrt{5}) = \pm 0.38$
95	$\Delta = \pm 2.776 \times (1.15/\sqrt{5}) = \pm 1.42$
99	$\Delta = \pm 4.604 \times (1.15/\sqrt{3}) = \pm 2.36$

Limits of Mean

	Lower	Upper
50	25.5	26.3
95	24.5	27.3
90	23.5	28.3

Thus based on the above samples, we could be 99 percent confident that the true mean is contained between 23.5 and 28.3.

### 7. Comparing Means (5,6,7)

7.1 The means of two sets of replicate observations can be compared by determining the estimate of the limits of the difference between the two means. If the limits include zero, the means are statistically alike; if they do not include zero, the means are different.

7.2 As an example, determine whether two heat treatments of Zircaloy-2 produce a significant difference in corrosion behavior. The heat treatments, corrosion data for 14 days in 750 F steam, and calculations of an estimate of the standard deviation, s, are presented in Table 8. An s for both measurements is calculated as follows:

$$s \stackrel{>}{=} \sqrt{(\Sigma \, d_1^{\, 2'} + \Sigma \, d_2^{\, 2})/[(n_1 - 1) + (n_2 - 1)]} = \sqrt{(5.29 + 24.35)/[(5 - 1) + (5 - 1)]} = 1.92$$

The s for both measurements is now multiplied by  $\sqrt{2}$ .

Corrected 
$$s = s(\sqrt{2}) = (1.92)(1.41) = 2.70$$

(s is multiplied by  $\sqrt{2}$  because differences increase s by  $\sqrt{2}$ .) The limits of the difference between the means is calculated from

$$\Delta = t (s/\sqrt{n})$$
  
Difference between means = 27.3 - 25.9 = 1.4  
s = 2.70  
n = 5

Degrees of freedom = (5 - 1) + (5 - 1) = 8From Table 7,

	50%	95%	99%
t =	0.706	2.306	3.355
$\Delta = \pm t \left( s / \sqrt{n} \right) =$	$\pm 0.85$	$\pm 2.79$	±4.05
Upper limit	2.2	4.2	5.4
		-1.4	-2.6

The above limits of the differences between the two means do not include zero in the first column so that the two means are statistically different at the 50 percent confidence level. The limits of the differences between the two means include zero in the last two columns and the two means are not significantly different at the 95 percent and 99 percent confidence levels.

7.3 An alternative method of comparing means has been described by Freeman (7) who uses the equation:

$$=\frac{\overline{d}}{\sqrt{(n_x s_x^2 + n_y s_y^2/n_x + n_y - 2)[(1/n_x) + (1/n_y)]}}$$

where:

1

 $\vec{d}$  = difference between the means of x and y,

 $n_x$  = number of variates of the x's,

 $s_x^2$  = variance of the x's,

 $n_y =$  number of variates of the y's, and

 $s_{y^2}$  = variance of the y's

The degrees of freedom are  $n_x + n_y - 2$ .

The calculated value of t is compared with the tabulated values of t (see Table 7) for the appropriate degrees of freedom. If the calculated value is larger than the value from the tables, the difference is significant at that confidence level. If the calculated value is smaller, the difference is not significant at that confidence level. For example, assume that the calculated t for two means obtained from five samples in each is 2.604. Then in Table 7 examine the values of t at 8 degrees of freedom (5 + 5 - 2). The calculated value 2.604 is greater than the tabulated value of 0.706 at the 50 percent confidence level and greater than 2.306 at the 95 percent confidence level, so that the means are significantly different at these levels. However, at the 99 percent confidence level the means are not significantly different because the calculated value of 2.604 is smaller than the tubular value of 3.355.

## 8. Comparison of Data on Probability Curves (8)

8.1 Data can be compared by plotting confidence limits for each curve on probability paper and determining whether they overlap. As an example, the log-probability distribution of stress-corrosion cracking endurance of aluminum alloys with and without silver additions are plotted in Fig. 6. Not all specimens failed. The estimate of standard deviation, s, is obtained from the plot as the difference between the log endurances at 16.2 and 50 percent probability. At the median (50 percent) the 95 percent confidence limits are calculated to be:

$$\pm t \left( s / \sqrt{n} \right)$$

where:

t =student's t (see Table 7), and

n = number of failed specimens,

At one standard deviation  $(\pm s)$  the limits must be expanded by adding  $\pm t(s/\sqrt{2n})$  to  $\pm t(s/\sqrt{n})$ . Lines through these points to the limits at the median establish approximate confidence limits.

8.2 Since not all specimens have failed,  $\pm t(s/\sqrt{n})$  is plotted one standard deviation from the median of specimens that have failed. This results in limits being rather broad at high and low probabilities, a consequence of lack of data in this region.

8.3 Although confidence limits overlap in Fig. 6, the lines from either sample are not included in confidence limits of the other; therefore, within the approximate range of probability of 2 to 50 percent, silver addition has a significant effect on stress-corrosion cracking.

### 9. Sample Size (9)

9.1 One of the most frequently asked questions in corrosion work is "How many samples should I test for each condition?" The statisticians usual answer is "What are the limits you wish to put on the results?"

9.2 Assume that it is desired to determine the corrosion behavior of a new alloy in a chemical environment and that prior tests with similar alloys have produced an estimate of the standard deviation (s) of 10 mg/dm². Furthermore, it is desired, at the 95 percent confidence level, that the limits that include the true value of the mean do not exceed 5 mg/

### dm². From Section 6 the desired equation is $\Delta = \pm t(s/\sqrt{n})$

where:

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asid

- $\Delta$  = limits that include the true value of the mean (at a particular level of confidence),
- t =student's t,
- s = estimate of the standard deviation, and

n = sample size. Thus,

$$\sqrt{n} = ts/\Delta$$
 or  $n = t^2 s^2/\Delta^2$ 

In the above equation, t is a function of n. For a first approximation assume that n = 16; then t = 2.131 (from Table 7).

$$n = (2.131)^2 (10)^2 / (5)^2 = 18.2$$

Substituting the value of t corresponding to a sample size of 18 and recalculating for n would give a more accurate value for n. Actually, the value of t for 18 samples at the 95 percent confidence level is not greatly different from that for 16 samples. Thus, under the above conditions it is estimated that a sample size of 18 would be required to assure that, at the 95 percent confidence level, the limits of the true value of the mean would not exceed  $\pm 5$  mg/dm² with an assumed estimate of the standard deviation of 10 mg/dm².

9.3 A reasonably small number of specimens can be used if a corrosion experiment is so designed that replicate specimens are exposed to an environment and specimens are removed periodically for evaluation (such as descaling). If there are, say, six to eight exposure periods, the removal of triplicate specimens at each period can furnish statistically significant results, by calculating a standard deviation based on all the data rather than for a single exposure period. That is, determine the mean for each exposure period; determine the difference, d, from the mean for the specimens at that exposure period; square the d's and determine the estimate of the standard deviation by the usual equation:

$$s = \sqrt{\Sigma d^2/(n-1)}$$

This approach assumes that the variances at the several exposure times are the same. The s determined by this method provides a better estimate of the standard deviation for a given exposure period than that obtained from the three replicate samples examined at each period.

9.4 On the other hand, extremely large sample sizes are required to obtain significant results if the evaluation is a go-no-go type, such as pitting versus no pitting or cracking versus no cracking. Snedecor has assembled probabilities for observation of these types. They are listed in Table 9. As an illustration assume that ten tubes were selected randomly from a heat exchanger and were examined thoroughly for stress-corrosion cracking. If cracks were found in only one of the ten tubes, it would be predicted at the 95 percent confidence level that between 0 and 45 percent of the remainder of the tubes would contain a stresscorrosion crack. On the other hand, if none of the ten tubes contained a crack that it would still be predicted at 95 percent confidence that between 0 and 31 percent of the remaining tubes would contain a crack. It can be seen from Table 9 that no cracks in 100 tubes would reduce the predicted percentage to 0 to 4 for the remainder of the tubes.

## 10. Comparison of Effects—Analysis of Variance (10)

10.1 The data presented in Table 10 are the results of laboratory impingement tests in 3 percent NaCl solution. Copper alloy specimens 1 by 4 by 0.05 in. were bolted radially to the periphery of nonmetallic disks. Each disk carried four specimens of each of four alloys. The maximum peripheral velocities of the outer edge of the specimens were 20, 25, and 40 ft/s. The test was run for 10 weeks and the maximum pit depth was obtained for each specimen. The whole test was then repeated. There were the following sources of variation: 4 alloys, 3 velocities, 2 tests, and 4 replicate specimens. There were the following main effects: "among alloys," "among velocities," "between tests"; the following two-way interactions: alloys-velocities, alloys-tests, velocities tests; one three-way interaction: alloysvelocities-tests; and an error term (derived from the variation among replicate specimens). The equations are:

For main effects.

SS = 
$$(1/n) \Sigma t^2 - (T^2/N)$$

For two-way interactions,

SS = 
$$(1/n) [(\Sigma t_1)^2 + (\Sigma t_2)^2 + \dots + (\Sigma t_2)^2] - [(T^2/N) + SS \text{ for each of the main effects}]$$

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For three-way interactions,

 $SS = (1/n) [(\Sigma t_1)^2 + (\Sigma t_2)^2 + \dots + (\Sigma t_2)^2] - [(T^2/N) + SS \text{ for all main effects and interactions}]$ 

For error term,

$$\Sigma t^2 - [(T^2/N) + SS$$

for all main effect and interactions] where:

SS = sum of squares,

- n = number of data within each level being compared,
- t = sum of data common to a given level of the main effect,
- $t_1$ ,  $t_2 \cdots t_z$  = test results common to a given combination of the levels of the two main effects (two-way interaction) or three main effects (threeway interaction). For example, in the alloy and test interaction  $\Sigma t$ 's is the sum of 12 data points for a given alloy and test and n = 12,
- T = sum of all the data, and
- N = total number of observations.

10.2 The sum of squares and mean square are determined for each main effect, two-way interaction, three-way interaction, and error term. The mean square, MS = SS/DF, where DF = degrees of freedom. The degrees of freedom are:

Tests: (2 - 1) = 1Alloys: (4 - 1) = 3Velocities: (3 - 1) = 2Tests-alloys:  $(2 - 1) \times (4 - 1) = 3$ Tests-velocities:  $(2 - 1) \times (3 - 1) = 2$ Alloys-velocities:  $(4 - 1) \times (3 - 1) = 6$ Tests-alloys-velocities:  $(4 - 1) \times (3 - 1) \times (2 - 1) = 6$ Error term: (96 - 1) - (the sum of the DF's of all main effects and interactions) = 72

10.3 The mean square for each effect is divided by the mean square of the most significant interaction containing that effect or the error if none of the interactions are significant. The result is compared with values from F tables which may be found in most text books on statistics (see Table 11). The F value is found by locating the degrees of freedom in the error term down in the table. If the calculated value is greater than the F value, the effect is significant. If it is less than the F value, the effect is not significant.

10.4 Calculation of the sum of squares and mean squares is shown in Table 12. Analysis

of variance is shown in Table 13.

### 11. Two-Level Factorial Design (8)

11.1 The two-level factorial design experiment is an excellent method for determining which variables have an effect on the outcome. The significance of each effect can be determined by analysis of variance.

11.2 As many variables as possible that may be expected to have an effect on the outcome should be included in the original experiment. In order to simplify the following example, only three variables will be used.

11.3 Assume that the stress-corrosion cracking endurance of aluminum alloys is being evaluated on alternate immersion tests in 3 percent NaCl. Suppose that one alloy contains silver and another does not, and in addition, that the effects of cold working and overaging are to be studied. The following nomenelature is then assigned:

A+ Alloy with silver A- Alloy without silver B+ With cold work B- Without cold work C+ With overage C- Without overage

	A	۸+	A-		
	B+	B	<b>B</b> +	<b>B</b> -	
C+					
C-					

11.4 This experiment requires eight entirely different sets of conditions. In order to determine the within-sample error more accurately, it is wise to replicate each condition. It is thus necessary to perform a minimum of 16 separate tests. In this particular example, the outcome is the log of the endurance of each stress-corrosion specimen.

	ŀ	4+		۹-
	B+	<b>B</b> -	<b>B</b> +	<b>B</b>
<u></u>	1.86	2.54	2.01	3.02
C+	1.95	2.43	2.32	2.89
C–	1.65	2.32	1.98	2.56
	1.73	2.25	1.87	2.60

Each response can be identified by its location. For example,  $y_{A+B+C+}$  has two responses, which are 1.86 and 1.95. They can

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be further subscripted as  $y_{A+B+C+1}$  and  $y_{A+B+C+1}$ . The error sum of squares for the experiment is:

$$\sum_{\substack{l \neq \mathbf{B} \pm \mathbf{C} \pm \\ l \neq j, k_1}}^{\mathbf{A} \pm \mathbf{B} \pm \mathbf{C} \pm} \left( \sum_{l=1^2} \left[ y(ijk)_l \right]^2 - \left[ \sum_{l=1^2} \left[ y(ijk)_l \right]^2 \right]^2 \right)$$

Each pair of responses must be squared, then added, and also added then squared. For example, the responses for A+B+C+ would be treated in the following manner:

$$(1.86)^2 + (1.95)^2 - \frac{1}{2} [1.86 + 1.95]^2 = 0.004$$

Each of these figures is then summed, to give the error sum of squares, which in this example is 0.0789. The error degree of freedom is (2 - 1) (8) = 8. The 2 is the number of times the response is replicated, and the 8 is the number of pairs.

11.5 In studying the effects of variables it is mathematically easier to work with differences between levels rather than with means at each level. The difference is referred to as a contrast:

$$\hat{\mathbf{A}} = (1/N) \left[ \Sigma y_+ - \Sigma y_- \right]$$

where:

 $\hat{A}$  = contrast or effect of silver,

N = number of tests, which is 16,

 $y_+$  = any response in the A + columns, and

 $y_{-}$  = any response in the A - columns.

**B** and **C** are calculated in a similar manner. The interactions AB, AC, BC, and ABC use the same procedure, except the signs for the responses are determined by products of the signs for the variables. For example, (A+)(B+) is AB(+) and (A+) (B+) (C-) is ABC-. For AB, A+B+ is (+), A+B- is (-), A-B+ is (-), and A-B- is (+). The absolute value of each response remains the same. Each effect or contrast has (2 - 1) degrees of freedom. The 2 is for the levels at each condition.

11.6 Each contrast is squared and multiplied by the number of tests (16) to obtain the sum of squares. Table 14 shows the values as they are used in analysis of variance. F is the ratio of the sum of squares of the effect to the error sum of squares. An F distribution table shows that for 1 degree of freedom for the greater sum of squares (numerator) and 8 degrees of freedom for the lesser sum of squares (denominator), the 5 percent and 1 percent levels of F are 5.32 and 11.25, respectively.

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Thus, in this example, there is less than 1 percent probability that the B effect is caused by random error. On the other hand, the remainder of the effects are not significant.

11.7 If this were a true problem, it would show that materials without cold work were not as susceptible to stress-corrosion cracking as materials with cold work. The addition of silver and overaging had no significant effect. Note that this is a hypothetical example.

11.8 Each time an additional variable is to be studied, twice as many experiments must be performed to complete the two-level factorial design. When many variables are involved, the number of experiments becomes prohibitive.

11.9 Fractional replication can be used to reduce the amount of testing. When this is done, the amount of information that can be obtained from the experiment is also reduced.

11.10 The example of the factorial design with three variables will be used. However, the negative side of the ABC contrast will not be included.

	A	+	<b>A</b> -			
	B+	<b>B</b> -	B+	B		
C	1.86			3.02		
C+	1.95			2.89		
6		2.32	1.98			
U		2.25	1.87			

11.11 With the previous method for analysis of variance it is found that ABC cannot be obtained, because the negative values are missing, and that contrasts  $\hat{A} = \hat{B}\hat{C}$ ,  $\hat{B} =$  $\overrightarrow{AC}$ , and  $\overrightarrow{C} = \overrightarrow{AB}$ . In this particular example, an assumption that all the interaction effects are unimportant is correct and it is possible to arrive at the same conclusions that were obtained from the full factorial design experiment. In some cases, it may be that the interaction effects are much greater than the effects of the main variables, in which case an assumption would lead to drastically wrong conclusions. It is wise to have some idea about the effect of interactions before fractional replication is used.

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47.

TABLE 1 Computing Standard Deviation

x	d	d²	x	d	ď²	x	d	ď²
190	13	169	178	1	1	178	1	1
195	18	324	162	15	225	164	13	169
169	8	64	162	15	225	189	12	144
185	8	64	171	6	36	178	1	1
180	3	9	192	15	225	171	6	36
178	1	1	172	5	25	172	5	25
170	7	49	195	18	324	156	21	441
179	2	4	181	4	16	185	8	64
= 177.17								
$=  x - \vec{x} $	$s = \sqrt{\Sigma d}$	$\frac{p}{(n-1)} = \sqrt{2}$	$\frac{642/23}{542/23} = 10.71$					

TABLE 2 P(%) = 100[(i - 0.375)/(n + 0.25)] = Cumulative Probability (see Fig. 2)

i	<b>P</b> (%)	Data	i	<b>P</b> (%)	Data	i	<b>P</b> (%)	Data
1	2.6	156 MDD	9	35.5	172 MDD	17	68.5	181 MDD
2	6.7	162	10	40	172	18	72.5	185
3	10.8	162	11	44	178	19	77	185
4	15	164	12	48	178	20	81	189
5	19	169	13	52	178	21	85	190
6	23	170	14	56	178	22	89.2	192
7	27	171	15	60	179	23	93.3	195
8	31.5	171	16	64.5	180	n = 24	97.4	195

TABLE 3 Endurances of Aluminum-5 percent Magnesium Stress-Corrosion Specimens Exposed Anodically in 3 percent NaCl Solution (see Fig. 3)

Intensiostatic 40 mA/in. ²	66, 90, 97, 108, 122,	70, 91, 97, 108, 122,	72, 91, 97, 110, 123,	73, 92, 99, 111, 126,	75, 92, 99, 115, 127,	75, 93, 100, 116, 128,	76, 93, 100, 116, 130,	77, 94, 100, 116, 130,	80, 94, 101, 116, 132,	80, 94, 106, 117, 133,	82, 95, 106, 117, 135,	82, 96, 106, 118, 135,	82, 96, 107, 119, 136,	88, 96, 107, 120, 140,	89, 97, 107, 122, 147,	
	Geor Mean Stan	netric n of log dard de	mean g ₁₀ end eviatio	urance n of lo	g ₁₀ end	lurance	= 10 = 2.0 = 0.0	3.2 )14 )844				<u> </u>				
Potentiostatic -0.34 V (S.C.É.) ^e	50, 67, 72, 76, 80, 84, 89, 97, 108,	52, 67, 72, 76, 80, 84, 90, 97, 112,	57, 68, 72, 76, 80, 85, 90, 98, 112,	60, 68, 72, 76, 80, 85, 92, 98, 115.	60, 69, 72, 76, 80, 85, 92, 99,	60, 69, 72, 76, 81, 85, 92, 99,	62, 70, 72, 77, 81, 85, 92, 99,	63, 70, 73, 77, 81, 86, 92, 99,	63, 70, 74, 77, 82, 86, 93, 99,	64, 70, 74, 78, 82, 86, 93, 100,	66, 70, 74, 78, 82, 86, 94, 100,	66, 71, 74, 78, 83, 86, 94, 100,	67, 71, 75, 78, 83, 87, 95, 102,	67, 71, 75, 78, 83, 88, 95, 105,	67, 71, 75, 78, 83, 88, 97, 105,	
-	Geor Mear Stan	netric n of lo dard de	mean g10 end eviatio	urance n of lo	: g ₁₀ end	lurance	= 80. = 1.9 = 0.0	15 0387 697								_

^a Saturated Calomel Electrode.

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 TABLE 4
 Ordered Maximum Pit Depths Developed on Alcan 3S-O Coupons Immersed in Kingston Tap Water for the Time Periods Shown Together with Their Ranks and Plotting Positions (see Fig. 4)

Rank	2 Weeks	Plotting Position	l Month	Plotting Position	2 Months	Plotting Position	4 Months	Plotting Position	6 Months	Plotting Position	l Year	Plotting Position
1	330	0.1000	570	0.0909	600	0.1000	620	0.0909	640	0.0909	700	0.0909
2	460	0.2000	620	0.1818	670	0.2000	620	0.1818	650	0.1818	70C	0.1818
3	500	0.3000	640	0.2727	770	0.3000	670	0.2727	670	0.2727	750	0.2727
4	500	0.4000	640	0.3636	790	0.4000	680	0.3636	700	0.3636	770	.3636
5	530	0.5000	700	0.4545	790	0.5000	720	0.4545	720	0.4545	700	0.4545
6	540	0.6000	740	0.5454	830	0.6000	780	0.5454	730	0.5454	810	0.5454
7	560	0.7000	780	0.6363	860	0.7000	780	0.6363	750	0.6363	820	0.6363
8	560	0.8000	810	0.7272	930	0.8000	800	0.7272	770	0.7272	830	0.7272
9	580	0.9000	840	0.8181	1030	0.9000	830	0.8181	780	0.8181	830	0.8181
10			910	0.9090			920	0.9090	850	0.9090	930	0.9090

### TABLE 5 Weight Gain of Zircaloy-2 in 750 F Steam at Time Indicated, mg/dm²

Days									
l	3	7	14	28	42				
9.8	11.8	20.3	25.6	34.8	47.2				
7.2	11.8	19.7	25.5	36.0	49.2				
6.6	10.5	19.0	24.3	34.1	47.3				
8.5	13.8	22.3	26.9	34.8	48.6				
9.9	13.9	22.4	27.1	41.7	52.2				

TABLE 6 Least Squares Calculation Zircaloy-2 in 750 F Steam

Log of time (x):	0	0.48	0.85	1.15	1.45	1.62
Log of weight gain (y):	0.99	1.07	1.31	1.41	1.54	1.67
	0.86	1.07	1.29	1.41	1.56	1.69
	0.82	1.02	1.28	1.39	1.53	1.67
	0.93	1.14	1.35	1.43	1.54	1.69
	1.00	1.14	1.35	1.43	1.62	1.72
$\Sigma x = 27.75$ $\Sigma y = 39.92$	$\Sigma xy = 41.303$	$\Sigma x^2 = 35.0015$				

TABLE 7 Distribution of t

.

Degrees	Probability					
Freedom	0.50	0.95	0.99			
1	1.000	12.706	63.657			
2	0.816	4.303	9.925			
3	0.765	3.182	5.841			
4	0.741	2.776	4.604			
5	0.727	2.571	4.032			
6	0.718	2.447	3.707			
8	0.706	2.306	3.355			
15	0.691	2.131	2.947			
30	0.683	2.042	2.750			
99	0.676	1.984	2.626			
×	0.674	1.960	2.576			

TABLE 8 Comparing Means—Zircaloy-2 for 14 Days in 750 F Steam

1450 F WC	2	1650 F WQ	
25.6	Mean = 25.9	25.5	Mean = 27.3
25.5	$\Sigma d^2 = 5.29$	26.8	$\Sigma d^2 = 24.35$
24.3	s = 1.15	26.8	s = 2.46
26.9		27.2	
27.1		30.5	
$s_{1,2}$ for both	n measurements		
= √(	$\Sigma d_1^2 + \Sigma d_2^2)/[($	$(n_1 - 1) + (n_2 - 1)$	$[1_2 - 1)]$
$=\sqrt{6}$	5.29 + 24.35)/[	(5 - 1) + (5 - 1)	(-1) = 1.92
Correct s =	$s_{1/2}(\sqrt{2}) = 1$	$92(\sqrt{2}) = 2.$	70

Number			Size of	Sample			Fraction	Size of	Sample
Observed, · X	10	15	20	30	50	100	• Observed, X/n	250	1000
0	0 31	0 22	0 17	0 12	0 07	0 4	0.00	0 1	0 0
1	0 45	0 32	0 25	0 17	0 11	0 5	0.01	04	0 2
2	3 56	2 40	1 31	1 22	0 14	07	0.02	i 5	1 3
3	7 65	4 48	3 38	2 27	1 17	18	0.03	16	24
4	12 74	8 55	6 44	4 31	2 19	1 10	0.04	27	35
5	19 81	12 62	9 49	6 35	3 22	2 11	0.05	39	47
6	26 88	16 68	12 54	8 39	5 24	2 12	0.06	3 10	58
7	35 93	21 73	15 59	10 43	6 27	3 14	0.07	4 11	69
8	44 97	27 79	19 64	12 46	7 29	4 15	0.08	5 12	6 10
9	55 100	32 84	23 68	15 50	9 31	4 -16	0.09	6 13	7 11
10	69 100	38 88	27 73	17 53	10 34	5 18	0.10	7 14	8 12
11		45 92	32 77	20 56	12 36	5 19	0.11	7 16	9 13
12		52 96	36 81	23 60	13 38	6 20	0.12	8 17	10 14
13		60 98	41 85	25 63	15 41	7 21	0.13	9 18	11 15
14		68 100	46 88	28 66	16 43	8 22	0.14	10 19	12 16
15		78 100	51 91	31 69	18 44	9 24	0.15	10 20	13 17
16			56 94	34 72	20 46	9 25	0.16	11 21	14 18
17			62 97	37 75	21 48	10 26	0.17	12 22	15 19
18			69 99	40 77	23 50	11 27	0.18	13 23	16 21
19			75 100	44 80	25 53	12 28	0.19	14 24	17 22
20			83 100	47 83	27 55	13 29	0.20	15 26	18 23
21				50 85	28 57	14 30	0.21	16 27	19 24
22				54 88	30 59	14 31	0.22	17 28	19 25
23				57 90	32 61	15 32	0.23	18 29	20 26
24				01 92	34 63	10 33	0.24	19 30	21 27
25				60 06	30 04	19 35	0.23	20 31	22 28
20				73 08	37 00	10 30	0.20	20 32	23 29
28				78 00	41 70	10 29	0.27	21 33	24 30
29				83 100	41 70	20 30	0.28	22 34	25 31
30				88 100	45 73	20 39	0.29	23 35	20 32
31				00 100	47 75	27 40	0.30	24 30	27 33
32					50 77	23 42	0.37	26 38	20 34
33					52 79	24 43	0.32	20 30	30 36
34					54 80	25 44	0.34	28 40	31 37
35					56 82	26 45	0.35	29 41	32 38
36					57 84	27 46	0.36	30 42	33 39
37					59 85	28 47	0.37	31 43	34 40
38					62 87	28 48	0.38	32 44	35 41
39					64 88	29 49	0.39	33 45	36 42
40					66 90	30 50	0.40	34 46	37 43
41					69 91	31 51	0.41	35 47	38 44
42					71 93	32 52	0.42	36 48	39 45
43					73 94	33 53	0.43	37 49	40 46
44					76 95	34 54	0,44	38 50	41 47
45					78 97	35 55	0.45	39 51	42 48
46					81 98	36 56	0.46	40 52	43 49
47					83 99	37 57	0.47	41 53	44 50
48					86 100	38 58	0.48	42 54	45 51
49					89 100	39 59	0.49	43 55	46 52
50					93 100	40 60	0.50	44 56	47 53

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TABLE 9 95 percent Confidence Interval (Percent) for Binomial Distribution

^a If X exceeds 50, read 100 - X = number observed and subtract each confidence limit from 100. ^b If X/n exceeds 0.50, read 1.00 - X/n = fraction observed and subtract each confidence limit from 100.

TABLE 10 Maximum Depth of Pitting, Mils

Velo-		Test 1			Test 2	
city, · ft/s	20	25	40	20	25	40
Alloy A	24	19	33	32	21	37
	24	18	35	27	20	44
	22	20	31	34	21	42
	23	21	34	26	19	43
Allov B	23	21	31	29	18	40
	22	19	36	32	21	37
	22	19	30	31	20	36
	20	19	33	27	20	38
Allov C	5	28	21	2	11	6
	4	30	19	3	9	8
	5	20	24	4	18	7
	5	23	18	3	13	6
Alloy D	10	3	7	6	7	11
	6	13	14	14	4	12
	10	4	8	11	6	12
	7	3	9	11	7	10

TABLE 11 Partial Table of the Distribution of F (5 percent)-Top (1 percent)-Bottom

DF of	DF of Effect MS									
Error MS	1	2	3	4	5	6	7	8	9	10
1	161	200	216	225	230	234	237	239	241	242
	4052	4999	5403	5625	5764	5859	5928	5981	6022	6056
2	18.51	19.00	19.16	19.25	19.30	19.33	19.36	19.37	19.38	19.39
	98.49	99.00	99.17	99.25	99.30	99.33	99.34	99.36	99.38	99.40
3	10.13	9.55	9.28	9.12	9.01	8.94	8.88	8.84	8.81	8.78
	34.12	30.82	29.46	28.71	28.24	27.91	27.67	27.49	27.34	27.23
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96
	21.20	18.00	16.69	15.98	15.52	15.21	14.98	14.80	14.66	14.54
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.78	4.74
	16.26	13.27	12.06	11.39	10.97	10.67	10.45	10.27	10.15	10.05
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.97
	10.04	7.56	6.55	5.99	5.64	5.39	5.21	5.06	4.95	4.85
25	4.24	3.38	2.99	2.76	2.60	2.49	2.41	2.34	2.28	2.24
	7.77	5.57	4.68	4.18	3.86	3.63	3.46	3.32	3.21	3.13
50	4.03	3.18	2.79	2.56	2.40	2.29	2.20	2:13	2.07	2.02
	7.17	5.06	4.20	3.72	3.41	3.18	3.02	2.88	2.78	2.70
70	3.98	3.13	2.74	2.50	2.35	2.23	2.14	2.07	2.01	1.97
	7.01	4.92	4.08	3.60	3.29	3.07	2.91	2.77	2:67	2.59
80	3.96	3.11	2.72	2.48	2.33	2.21	2.12	2.05	1.99	1.95
	6.96	4.88	4.04	3.56	3.25	3.04	2.87	2.74	2.64	2.55
100	3.94	3.09	2.70	2.46	2.30	2.19	2.10	2.03	1.97	1.92
	6.90	4.82	3.98	3.51	3.20	2.99	2.82	2.69	2.59	2.51
×	3.84	2.99	2.60	2.37	2.21	2.09	2.01	1.94	1.88	1.83
	6.64	4.60	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32

$T^2/N =$	$(1811)^2/96 = 34163.76041$	
SS for tests =	$\frac{1}{48}[(895)^2 + (916)^2] - T^2/n$ 4.59375	DF = 1 MS = 4.59375
SS for alloys =	$\frac{1}{24}[(670)^2 + (644)^2 + (292)^2 + (205)^2] - T^2/N$ 7124.78125	DF = 3
SS for velocities =	$\frac{1}{32}[(524)^2 + (515)^2 + (772)^2] - T^2/N$	MS = 2374.92708
=	1329.52084	DF = 2 MS = 664.76042
SS for tests-alloys =	$\frac{1}{2}[(304)^2 + (366)^2 + \ldots + (111)^2] - [T^2/N + 4.59375 + 7124.78125]$	
=	811.78125	DF = 3 MS = 270.59375
SS for tests-velocities =	$\frac{1}{16} \left[ (232)^2 + (280)^2 + \ldots + (389)^2 \right] \\ - \left[ T^2 / N + 4.59375 + 1329.52084 \right] \\ 172.31250$	DF = 2 MS = 86.15625
SS for alloys-velocities =	$\frac{1}{6}[(212)^2 + (159)^2 + (299)^2 + (206)^2 + (157)^2 + (281)^2 + (31)^2 + (152)^2 + (109)^2 + (75)^2 + (47)^2 + (83)^2]$	
=	$- [T^2/N + 7124.78125 + 1329.52084]$ 1924.56250	DF = 6 MS = 320.76041
SS for tests-alloys-velocities =	$\frac{1}{2}[(93)^2 + (78)^2 + \ldots + (45)^2] - [T^2/N + 4.59375 + 7124.78125 + 1329.52084 + 811.78125 + 172.31250 + 1924.56520]$	
=	129.43750	DF = 6 MS = 21.57291
SS for error =	$[(24)^2 + (24)^2 + (22)^2 + \ldots + (10)^2]$ $[T^2/N + SS \text{ for all main effects} and interpretional$	
=	438.2500	DF = 72 MS = 6.08680

الله G 16 TABLE 12 Calculations Based on Section 10 and Examples of Table 10

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TABLE 13 Analysis of Variance

			95 percent Level		99 percent Level	
	Freedom	MS Ratio	F Value	Signi- ficant?	F Value	Signi- ficant?
Tests	1 3	4.59375	10.13		34.12	no
Tests, Alloys	1,5	270	10.15	no	54.12	
Alloys	3.6	2374.92708 _ 7.45	4 76	Ves	9.78	
Alloys, Velocities	5,0	320	4.70	yes	7.70	no
Velocities	2.6	664.76042 - 2.07	5 14	80	10.92	<b>P</b> O
Alloys, Velocities	2,0	320	2			
Tests, Alloys	3.6	$\frac{270.59375}{-12.5}$	4 76	ves	9.78	ves
Tests, Alloys, Velocities	3,6	21.57		,		,
Tests, Velocities	2.6	$\frac{86.15625}{$	5 14	80	10.92	<b>B</b> O
Tests, Alloys, Velocities	2,0	21.57	5.14			
Alloys, Velocities	6.6	$\frac{320.76041}{$	4 28	ves	8 47	ves
Tests, Alloys, Velocities	0,0	21.57	7.20	903	0.47	<b>,</b>
Tests, Alloys, Velocities	6 72	$\frac{21.57291}{21.57291} = 3.54421$	2 23	ves	3.07	Ves
Error	0,72	6.08680	2.05	, ••	5.07	500

### TABLE 14 Analysis of Variance

Effect	Contrast	Sum of Squares	Degrees of Freedom	F
Â	-0.1575	0.397	1	5.03
Ê	-0.3275	1.716	1	21.75
Ĉ.	+0.1287	0.265	1	3.36
ÂB	+0.0337	0.018	L	0.23
ÂĈ	-0.025	0.010	1	0.13
BC	-0.013	0.0028	1	0.04
ABC	+0.0188	0.0056	1	0.07
Error		0.0789	8	



FIG. 1 Normal Distribution Curve.

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Sample Mean  $\bar{x} = 177.17$ Standard Deviation s = 10.71



FIG. 2 Cumulative Frequency Distribution of 24 Corrosion Tests (see Table 2).



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FIG. 3 Endurance of Aluminum-5 Percent Magnesium Alloys Exposed Anodically in 3 Percent NaCl Solution (See Table 3).



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FIG. 4 Maximum Pit Depth Data for Alcan 3S-O (AA3003-O) Immersed in Kingston Tap Water for the Time Periods Shown Plotted Against Their Cumulative Relative Frequencies (See Table 4).



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FIG. 5 Zircaloy-2 Exposed to 750 F-1500 psi Steam.



Confidence limits code:

Begion within 95 percent confidence limits on best fit line for endurances of alloys containing silver
Region within 95 percent confidence limits on best fit line for endurances of alloys without silver

Region common to both

FIG. 6 Effect of the Addition of Silver on Stress-Corrosion-Cracking Behavior of 7079 Type Aluminum Alloys.

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