The Corrosion of Metals—I. Mechanism of Corrosion Processes

By R. M. BURNS

This paper outlines the application of electrochemical methods to corrosion investigations. It discusses the position of the potential of a metal against its environment and the trend of this potential with time, pointing out that it is thereby possible to determine whether the corrosion process is controlled by reactions occurring at the anodic areas, the cathodic areas, or both; that is, whether there is a tendency toward passivity, inhibition or progressive attack. Measurements of film stability whether in terms of the leakage current which may be passed through the film or in terms of the amount of film forming material required to produce passivity or the amount of film destroying material required to render a metal active, furnish information as to the quality of corrosion resistant films. Measurements of the rate at which a film forms on a metal when placed in a film-forming environment throws light on its relative surface reactivity, and such information is of assistance in determining the rate of corrosion in homogeneous corrosive environments or the rate of passivation in the film-forming environments. On the basis of such measurements and with a chemical knowledge of the environments in which metals are used as well as the composition and physical state or structure of the metals, it is possible to predict corrosion behavior and to obtain an understanding of corrosion problems usually not possible by ordinary empirical corrosion tests.

ALL metals are corrodible under the appropriate circumstances. The most important metal industrially, iron, is probably the most corrodible under ordinary conditions. Many estimates have been made of the value of iron and steel products destroyed by corrosion.[1] While much depends upon the basis of calculation it seems reasonable to conclude that the annual cost of corrosion in this country is of the same order as the interest on the public debt or nearly one third of the cost of the federal government in normal times. The common non-ferrous metals—zinc, lead, copper, aluminum, nickel and tin—are more resistant to corrosion largely because of their tendencies to form protective surface films. In the atmosphere under favorable circumstances tests have indicated, for example, that in the form of sheet 0.03 inch in thickness and exposed on one side as in the case of roofings, zinc, copper and lead if mechanically undisturbed would resist corrosion for more than one, two and three centuries respectively.[2] Once a protective film is formed it may preserve the metal indefinitely. Under other circumstances these metals may readily corrode. Contact with large inert soil particles may result in the perforation of cable sheathing 0.10 inch in thickness in about 8 years.[3] Tin, although resistant to corrosion in air and pure water, is severely corroded by alkalies, and aluminum is attacked by both alkalies and acids. The

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noble metals such as gold, silver and platinum, being less reactive chemically than the more basic metals, are as a group the least corrodible, yet silver tarnishes markedly in moist atmospheres containing volatile sulfur compounds; gold is attacked by halogens in solution and platinum by fused alkalies.

The protection of metals from corrosion may be accomplished in general either by maintaining a non-corrosive surrounding environment or by coating the metallic parts with paints, lacquers or more corrosion-resistant metals. Such measures as the control of humidity and dust in interior atmospheres, deoxygenation of boiler waters, the use of passivators such as chromates, carbonates, phosphates, silicates and alkalies in the water-cooling systems or water scrubbers of air conditioning equipment and the use of cathodic protection which consists in setting up an electrolytic cell in which the metallic part subject to corrosion is made the cathode, are typical examples of environmental control designed to inhibit corrosion. Another well-known example of avoiding corrosion by control of environment is the protection of underground cables which is afforded by the proper drainage of electrical stray currents which have been picked up by the cable network. Where it is infeasible to maintain an inert environment the use of non-ferrous metallic coatings is of great value in the preservation of steel products. Much metallurgical work has been devoted in recent years to the development of corrosion-resistant alloys. In both of these cases the protective feature consists in a naturally developed surface film. Where natural films afford insufficient protection it becomes necessary to resort to coatings of organic materials such as paints, lacquers, enamels, complex structures of such materials as pitches or asphalts with jute felt or paper, etc. It has been estimated that one hundred and twenty million gallons of paint are used annually for corrosion prevention.[4]

Corrosion may be defined in most general terms as the chemical reaction of a metal with the non-metallic constituents of its environment. In this sense any reaction in which a metal is degraded to one of its compounds, such as an oxide, hydroxide, acid or salt is a corrosion reaction. The nature of the reaction which occurs in any given case depends both upon the reactivity of the metal, its purity, physical state and surface condition and upon the character of the environment, that is, upon the chemical components present, their physical phases and concentrations. It also depends upon the temperature. Corrodibility is not wholly an inherent property of a metal which can be determined by a single arbitrarily chosen corrosion test of any sort; even the relative order of corrodibility of a series of metals

is not constant.[5] For example, iron, magnesium and zinc corrode in conductivity water exposed to the air in the order given; in sodium chloride solution the order is magnesium, zinc and iron, while finally in strong alkali solutions these metals corrode in the order: zinc, iron and magnesium.

It is apparent that the occurrence of corrosion depends upon both the character of the environment and of the metal.   While the environment in which a metal is used is usually complex, it is generally possible to recognize those constituents which exert a controlling influence on the course of corrosion.   In the ordinary atmosphere water vapor and oxygen are major factors in the process.   Other substances such as sulfur dioxide, chloride ions and dust also influence the character of the corrosive attack.   The green patina, a basic sulfate, which forms in the course of time on copper exposed to the air and which may preserve the metal for centuries, owes its origin to traces of sulfur dioxide in the atmosphere.[6] On the other hand, the higher concentrations of sulfur dioxide prevailing in the neighborhood of smelters which treat sulfur bearing ores may rapidly corrode copper telephone wires to destruction. Steel containing up to 0.25 per cent copper is about two-fold more resistant to corrosion than non-copper bearing steel in most industrial atmospheres; in New York City, however, the very small chloride ion content of the atmosphere, an otherwise typical industrial atmosphere, largely destroys the corrosion resistance conferred by the copper. Rainfall is an influential factor in the corrosion of metals exposed to the atmosphere.   It may increase corrosion by removing soluble corrosion products from the surface of the metal, or it may retard corrosion by washing away dust particles and electrolytes, both of which promote corrosive attack.   For example, in New York City the daily application of a water spray increased the rate of corrosion of zinc by 30 per cent but decreased the rate of corrosion of different ferrous materials from 30 per cent to 46 per cent, the amount of corrosion being determined by loss of weight measurements.   The corrosion products of zinc are appreciably more soluble than those of iron and presumably were largely removed by the frequent washing.   On the other hand, the deliquescent nature of the corrosion products of iron [7] at humidities prevailing a large part of the year provide, in contrast to the relatively less deliquescent corrosion products of zinc, a film of moisture more or less saturated with corrosive electrolytes and dust particles.   This film is diluted or otherwise removed by the water spray.

Indoor environments differ from the outside atmosphere mainly in being drier, cleaner and subject to less pronounced temperature varia-

tions. As a consequence, metals corrode somewhat less rapidly indoors but the character of the attack generally resembles that shown out of doors. Underground exposures to soils and waters are often severe and cause ferrous structures to fail unless protective non-metallic coatings are employed. Considerable progress has been made within the past ten years in determining the corrosivity of soils and developing adequate preservative coatings.[8]

The best measure of the tendency of a metal to corrode is, in thermodynamical terms, the decrease in free energy which accompanies the chemical reaction involved in the process, i.e., the difference in energy between the initial and final state of the system. This may be obtained by simple calculation and is of value in showing whether or not it is possible for corrosion to occur under the conditions defined. There is no assurance however, that reactions which are possible will actually take place within a reasonable time, if at all. Calculations [9] show that, exposed to the atmosphere containing moisture, aluminum, zinc, tin, iron, nickel, copper and silver may corrode to their respective hydroxides. If, oxygen be excluded the last three metals listed cannot corrode and iron only to the lower state of oxidation. These calculations, however, give no information as to the rate of corrosion or the mechanism by which it takes place, matters of great practical importance.

The rate of corrosion or of any other chemical reaction bears no direct relationship to the energy changes involved; it cannot be predicted but must be measured in some form.[10] Obviously the rate of corrosion depends upon the nature of the chemical reactions at the surface of the metal. Generally, secondary reactions are involved and the slowest step in the process controls the rate. The limiting factor is usually some sort of barrier,—a film of gaseous or solid corrosion products at the surface.

The mechanism by which corrosion occurs may be one either of direct combination of the metal and non-metal or the replacement by the corroding metal of hydrogen or another metal in compounds. The oxidation of metals, particularly at higher temperatures, halogenation reactions, such as the chlorination of aluminum, and the reaction of copper and sulfur, are examples of direct combination. In many of the reactions which occur in the atmosphere, such as the formation of tarnish films, the processes are somewhat obscure. When zinc corrodes in the ordinary atmosphere an oxide film forms in the early stages which is pseudomorphic with the metal [11] but which is converted eventually into the ordinary granular form of zinc oxide. The rate of corrosion of zinc is determined by the rate of this conversion

process,[12] the granular oxide film having no retarding influence.   This
is shown by the linear relationship in Fig. 1 which compares the cor-
rosion-time curves for zinc, copper, lead, and iron in the atmosphere.
In this case corrosion is expressed in terms of weight gain due to the
accumulation of corrosion products.   It will be observed that the re-
lationship for copper is a parabolic one, indicating that the process is
controlled by the rate of diffusion of oxygen through the increasingly
thicker oxide film.   Up to a thickness of about 10 Å the film is invisible
and when formed in pure air is impervious to volatile sulfur compounds.
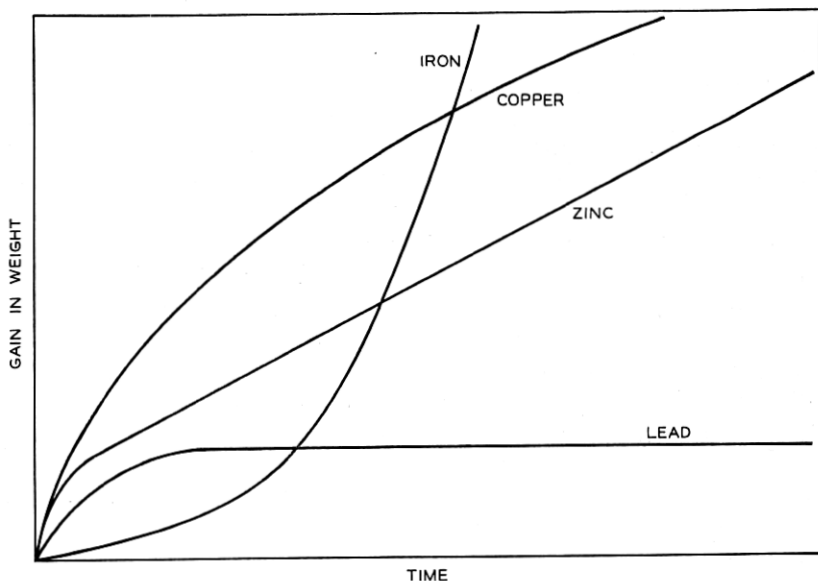

Fig. 1—Corrosion-time relationships characteristic of certain metals exposed to the
atmosphere.

A third type of corrosion-time curve represented by lead becomes
parallel with the time axis after the initial stages.   Evidently the film
in this case is impervious to the constituents of the environment.
The curve given for iron indicates that the film which forms in the
initial stages of the exposure exerts an accelerating influence upon
the subsequent rate of oxidation.

It should be mentioned that this acceleration occurs only at
humidities above what has been called the "critical" humidity.   By
this term is meant the relative humidity corresponding to the vapor
pressure of a saturated solution of the corrosion products, which de-
pends upon the composition and to some extent the structure of these

products. For iron this is somewhere between 40 and 65 per cent
relative humidity, probably nearer the latter figure.[13] The atmos-
pheric corrosion products of the non-ferrous metals are in general less
deliquescent, i.e., have higher critical humidities; for nickel it appears
to be above 70 per cent relative humidity and for zinc and copper
above 75 per cent. It has been suggested that the marked increase in
the resistance of copper containing about 0.5 per cent arsenic to atmos-
pheric corrosion is due to the fact that the presence of arsenic renders
the corrosion product less hygroscopic.[14] The effect of copper in
copper bearing steel may be of the same nature;[15] apparently the
inhibiting action in this case does not lie in the production of a film
which is any more resistant to attack initially than that on ordinary
steel.[16] In dust-free air, even at high humidities, iron does not corrode
but forms an invisible protective film. Electron beam studies [17]
have indicated the structure of this film to be a form of ferric oxide
which has been designated as $\alpha\ Fe_2O_3$ in contrast to the composition
of a non-protective form which appears to be $\gamma\ FeO \cdot OH$.

The presence of dust particles in the atmosphere greatly increases
the rate of corrosion of iron. In this case, as well as in the accelerated
attack which occurs above the point of critical humidity, the process
involves the displacement of hydrogen from water. Other common
examples of this type are the solution of metals in acids or alkalies,
the reaction of sodium with water, the deposition of metallic copper
from copper sulfate solution by metallic zinc and in general the
corrosion of metals in moist air, in soils and in water. It is well estab-
lished that the process of corrosion in these cases is electrolytic in
character, i.e., that corrosion occurs by means of the operation of small
galvanic cells at the surface of the metal. The primary reactions of
these cells may be and generally are followed by important secondary
chemical reactions of the products of electrolysis with the constituents
of the environment. Between the anode and cathode areas there is a
flow of current through intervening electrolytic paths of greater or
lesser resistance. Naturally the amount of corrosion is proportional
to the amount of current flow.[18] It is largely the distribution and size
of anode areas which determines the character of the corrosive attack.
For a given amount of metal dissolution the existence of relatively few
anode areas small in size obviously leads to pitting, while if there are
numerous anodes uniformly distributed, corrosion will likewise be
uniform. The distribution of anodes is determined by the inhomo-
geneity of the base metal, the character of the films which are formed,
the accidental contact of inert bodies and the conductivity of the sur-
rounding electrolytic media.

The potential differences which are responsible for the existence of corrosion cells arise either from some chemical or physical inhomogeneity of the metal or from some inhomogeneity of the environment at the metal surface. These cells or galvanic couples provide the means whereby the natural tendency of metals to corrode may express itself. The nature of the electrodes composing some of these electrolytic cells is given in the following table:

Cathode	Anode	Example of Cell
Noble metal	Base metal	Two-phase alloys, metal containing metallic impurities, two metals in contact or metal with porous metal coating.
Metal oxide	Metal	Iron with porous oxide scale.
Dust	Metal	Iron with carbonaceous dust particles on surface.
Metal freely exposed to oxygen	Metal in diminished oxygen supply	Exclusion of air at point of contact of metal and inert material or decreased oxygen concentration at bottom of pits on surface of metal.
Metal in concentrated acid, alkali or salt solution	Metal in dilute acid, alkali or salt solution	Metal in contact with solution of two different concentrations or two different solutions.
Annealed or coarsely crystalline metal	Same metal strained or of small crystal size	Metal which has been subject to non-uniform heat treatment or cold working.

It will be observed that there are ample possibilities for a metal of even high purity to corrode. The existence of more than one metallic phase in metals in industrial use often does not have a significant bearing upon their corrosion behavior. For example, studies conducted by these Laboratories have shown that high purity lead, lead hardened with 1 per cent antimony, 3 per cent tin or 0.03 per cent calcium, when used as cable sheathing show approximately the same resistance to corrosion. While one of these materials may be somewhat more corrodible than others in a given natural environment, the reverse will be true for another set of conditions. The environment is of far greater importance than the composition of the sheathing and consequently the control or avoidance of corrosion is attained by maintaining the cable plant in non-corrosive surroundings.

Of the types of corrosion cells listed above, those due to concentration differences in the surrounding medium are among the most prevalent. Differential aeration is one of the most common causes of corrosion. Lead is corroded beneath the point of contact with a large grain of sand when in an atmosphere containing oxygen and water vapor.[19] The point of contact is less accessible to oxygen than surrounding parts. The potential of this cell is somewhat less than 0.1 volt, the value determined in these Laboratories for the difference between the

potentials of lead in identical solutions exposed respectively to oxygen and to an inert gas, nitrogen. An even more striking example of the operation of oxygen concentration cells is observed when glass beads are in contact with a lead surface wet by a film of sodium chloride solution exposed to the air.[20] After a period of a few months a ring of bright red corrosion product forms around an anodic pit located directly beneath each bead. This red corrosion product, a red tetragonal form of litharge, is characteristic of an alkaline attack. Apparently sufficient caustic soda to cause corrosion (a solution of pH 12 approximately) was produced by the differential aeration cell resulting from the contact of the bead with lead.

The foregoing paragraphs have described some of the complexities encountered in corrosion processes. In view of these complexities it has been one object of these Laboratories for some years to advance the development of a generalized theory of corrosion applicable to all cases of corrosion of the replacement type, since it is this type of process which prevails in atmospheric, soil and water exposures. Direct combination of metals with non-metallic elements is limited largely to somewhat extreme conditions such as those of industrial processing. Attention will now be directed to the general theory of corrosion in its present state of development.

The fundamental reactions of corrosion processes of the replacement type as represented by the operation of corrosion cells are as follows:

$$\text{At the anode: } M \xrightarrow{-e} M^+; \; 2(OH)' \xrightarrow{-2e} O + H_2O.$$
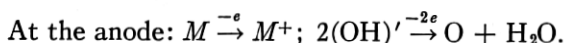
That is, the metal sends ions into the solution or there are plated out non-metallic elements such as oxygen. Either process is accompanied by a loss of electrons. If corrosion is induced by an externally applied potential, as for example when stray electrical currents flow from underground metallic structures to earth, oxygen atoms may leave the surface in the form of molecular oxygen.

$$\text{At the cathode: } M^+ \xrightarrow{e} M; \; H^+ \xrightarrow{e} H; \; 2H \to H_2 \text{ gas.}$$
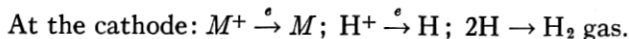
This process consists in plating out either metal or hydrogen atoms. In the latter case atomic hydrogen either leaves the metal surface as hydrogen molecules or acts as a reducing agent, being in turn oxidized. The electrode reactions may be combined in equations as follows:

1. Solution of the metal: $M + H^+ \to M^+ + H$.
2. Removal of hydrogen: (*a*) $2H \to H_2$,
   (*b*) $2H + O \to H_2O$.

The corrosion reaction represented by the first reaction automatically stops when the metal surface becomes covered with hydrogen atoms and can only proceed when and as hydrogen is removed by one of the processes above given. Some metals evolve molecular hydrogen if the potential of the corrosion cell is slightly over that required to plate out hydrogen atoms. In the greater number of cases, however, molecular hydrogen is not liberated rapidly, i.e., as bubbles, unless the potential is substantially higher than that required to plate out the atomic form. The additional potential required to evolve molecular hydrogen against the normal atmospheric pressure is termed "overvoltage." In the case of metals of high hydrogen overvoltage, oxygen or oxidizing substances are required to facilitate the removal of the hydrogen film if corrosion is to proceed at an appreciable rate. Consequently corrosion may be controlled by the rate at which oxygen reaches the metal surface and "depolarizes" it. In many cases both processes are operative. For example, when iron is corroded in dilute potassium chloride solutions it is interesting to note that under a pressure of one atmosphere of oxygen 1/13 of the total corrosion is accompanied by the discharge of hydrogen gas and 12/13 by the oxidation of hydrogen to form water. When the oxygen pressure on the system is raised to 25 atmospheres by conducting the experiment in a closed bomb the total rate of corrosion is increased 45-fold owing to the increased rate of hydrogen oxidation, the rate of hydrogen evolution being practically unaffected. In practical cases, as would be expected, either the character of the corroding medium or the purity of the metal may affect this ratio of hydrogen control to oxygen control. In tests in which iron specimens were totally immersed in sea water exposed to oxygen, about 35 per cent of the total corrosion was accompanied by hydrogen evolution, whereas for similar specimens in a half-normal solution of pure sodium chloride (which corresponds roughly to the salt content of sea water) only 5.6 per cent of the corrosion was of the hydrogen evolution type.[21] The presence of one part per million of impurity in zinc considerably accelerates the rate of corrosion [22] mainly by stimulation of hydrogen evolution.

The intensity with which a metal tends to send metal ions into solution increases with the basic character of the metal. The presence of ions of the metal in the solution may be considered to constitute a force opposing this ionization tendency and the value of the resulting equilibrium is known as the potential of the metal in that solution. The value is constant or static only so long as there is no flow of current between the metal and solution. The molal potentials and normal potential of metals are their static potential in solutions of

their salts in which the metal ion concentrations are molal and normal respectively. A table of the values of such potentials constitutes the so-called E.M.F. series. This comparison of metals is of little value in predicting either the driving force or the rate of operation of practical corrosion cells, the electrodes and ionic concentrations of which bear little correspondence to those defined in the E.M.F. series. Moreover, the practical case is complicated in many instances by the gas electrode behavior of the metal and by the flow of current during the corrosion process. For example, the potentials of many metals when measured in the atmosphere are much more noble or cathodic than might be expected from a knowledge of the E.M.F. series. This is due to the fact that in the presence of moisture and oxygen, metals may function wholly or in part as oxygen electrodes. The exact values of these electrodes depend upon the concentrations of oxygen present, and upon the acidity of the solution. This explains the origin of the potential difference of the differential aeration cells to which reference has been made previously.

If the corrodibility of copper in the presence of moisture were judged solely from the position of the metal in the E.M.F. series no attack would be expected, since in this series copper is more noble than hydrogen, the element which must be displaced in the corrosion process. As a matter of fact copper does not corrode even in hydrochloric or sulfuric acids in the *absence of available oxygen*. It is readily corrodible, however, in nitric acid because in effect under these circumstances the position of the hydrogen electrode is rendered cathodic to copper (i.e., more noble than copper) owing to the depolarizing influence of oxygen. It is probably for this same reason that oxygen markedly accelerates the corrosion of monel metal in 3 per cent sulfuric acid.[23]

The change in electrode potential with current flow, polarization, may be illustrated in a simple experiment as follows: If the zinc coating is removed from a portion of the surface of a strip of galvanized iron, exposing thereby the underlying iron surface, one has what amounts to a simple galvanic zinc-iron couple. If this couple is completely immersed in a dilute salt solution and potential measurements are made at different points on the iron and zinc surfaces by means of a calomel half-cell, it will be observed that the potentials of iron and zinc at some distance from the iron-zinc interface are approximately those values obtained for these metals separately in the same electrolyte; while, on the other hand, the value of the iron potential near the interface has become more anodic and the potential of zinc near the interface has moved in the cathodic direction, i.e., the difference in potential between iron and zinc near the interface of the two metals is appreci-

ably less than when taken at points more widely separated. Figure 2 gives a schematic representation of this experiment. The change in potential is the result of current flow through the electrolyte from zinc to iron. The current densities are highest in the region of the interface, the metal ion concentration becoming increased at the anode area and decreased at the cathode area, producing thereby anodic and cathodic polarization, respectively.

This polarization behavior of corrosion cells largely determines the rate of corrosion. It is obvious that the effective potentials of corrosion cells may be reduced by polarization to zero, in which case the rate of corrosion is limited to that required to maintain this polariza-
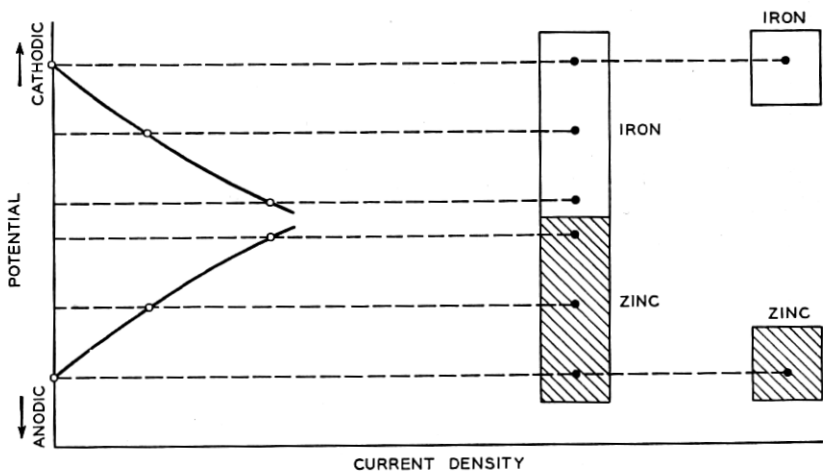

Fig. 2—Illustration of galvanic polarization.

tion. In other words, the progress of corrosion may be controlled by the extent either of anode polarization or cathode polarization or both, that is, either one may determine the final result. Figure 3 represents the variety of current density-potential relationships which may exist in corrosion cells. In Cell 1, in which there is no appreciable polarization of either anodic or cathodic areas (as indicated by the small change of potential with current), corrosion current flow is limited by the resistance of the electrolytic paths between anodes and cathodes and since this may be small if these areas are contiguous the corrosion rate may be high. In Cell 2 the anode is highly polarized as represented by the solid line or progressively less polarized as the point of intersection with the non-polarized cathode occurs at higher and higher current densities as represented by the dotted lines. In a

similar way Cell 3 shows cathode polarization only and Cell 4 both anode and cathode polarization. Since the rate of corrosion is proportional to the flow of current per unit area it is obviously limited in the last three cases by the values of current density at which the polarization curves intersect. In the presence of adequate oxygen or in cases where hydrogen is readily discharged corrosion cells are likely to resemble Cell 1. Where this is not the case, as in the absence of oxygen or where the cathodes have high values for hydrogen overvoltage, the result will be as shown for the cathodically polarized Cell 3. The presence of an inhibitor such as a positively charged colloid or
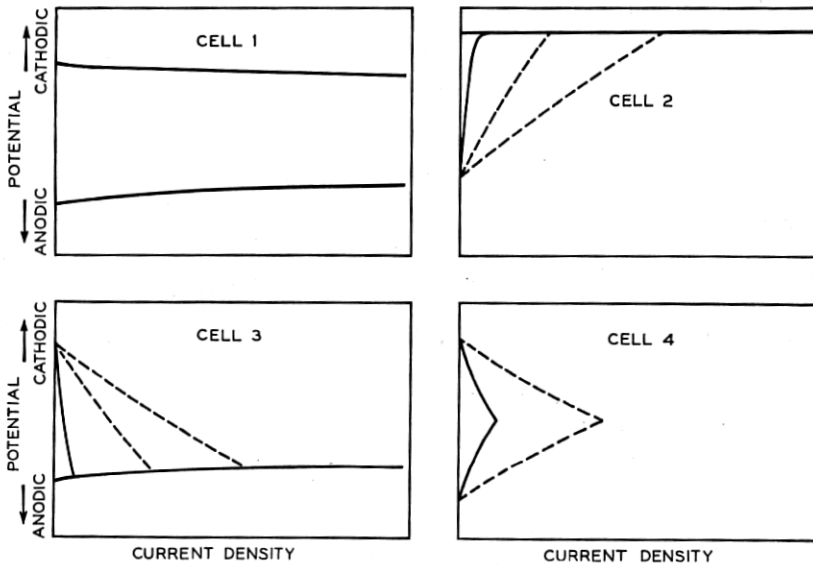

Fig. 3—Types of polarization in corrosion cells.

the amalgamation of the metal surface with mercury are other conditions which promote cathode polarization. On the other hand, the action of passivating agents such as chromates, silicates and in some cases sulfates, carbonates, etc., is to produce anodic polarization as in Cell 2. It will be observed that whereas in the presence of inhibitors of the type mentioned above which polarize the cathode the resulting potential of the corrosion cells and therefore of the metal specimen as a whole should move in the anodic direction as the process of inhibition takes place, in the case of passivating agents (which influence anode processes) the effect of increasing passivation is a trend of potential in the cathodic or noble direction. In both cases corrosion is retarded or prevented entirely.

The manner in which the conductance of the surrounding electrolyte influences the rate of corrosion is illustrated in Fig. 4A in which the upper curve represents the cathodic and the lower the anodic polarization. Assuming equal anodic and cathodic areas the corroding current density for the lower conducting solution is represented by "M" and that for the higher conducting solution by "N." In the actual case where anodes and cathodes are in close juxtaposition, the internal resistance is low and consequently the corroding current density approaches that represented by the intersection of the polarization curves.
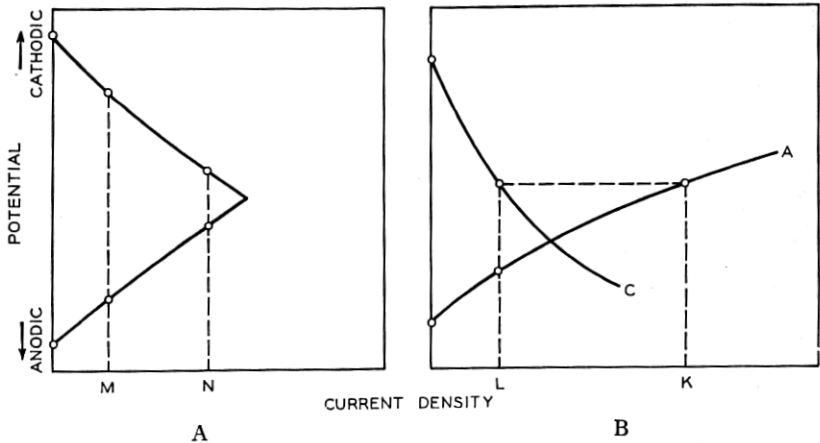

Fig. 4—Effect of conductance and of electrode area on corrosion current densities.
    M = Lower conducting solutions.
    N = Higher conducting solutions.
    L = Corrosion current density for cells of equal cathode and anode areas.
    K = Corrosion current density when ratio anode area to cathode is small.

Thus far consideration has been confined for the sake of simplicity to corrosion cells in which the anodic and cathodic areas are equal. Usually in actual experience this is not the case. In corrosion characterized by pitting, the anodic area is generally small compared to the cathodic areas. This situation is illustrated in Fig. 4B in which it will be seen that under these conditions a high corroding current density corresponding to a rapid rate of attack may occur. Conversely, in cases where the ratio of anode areas to cathode area is large, the rate of attack will be small, being thus controlled by cathodic polarization. In this connection it may be of interest to consider the effect of impurities upon rate of corrosion. If the contaminating metal is anodic and exists as a separate phase it will tend to dissolve with the formation of small pits which having once formed may possibly

continue to function as the anodes of oxygen concentration cells. If, on the other hand, the metallic impurity is cathodic and present as a separate phase, corrosion will be rather more uniform in character and its rate will be controlled in the absence of oxygen by the ability of the impurity to discharge hydrogen. Unless its overvoltage is low, that is, unless it discharges hydrogen readily, the rate of corrosion will be slow, the corrosion cells being polarized cathodically. The presence of oxygen or oxidizing agents under these conditions will depolarize these cathodic areas and accelerate corrosion.

From the foregoing it is apparent that a knowledge of the anodic and cathodic current density potential relationships which are established on the surface of a metal in a given environment would make possible an understanding of the processes which are taking place and lead to a prediction of corrosion behavior. It is generally impossible to measure these quantities as they relate to individual corrosion cells owing to a lack of knowledge of the electrode areas involved. Probably these comprise a wide range of sizes and change in size with the progress of corrosion. Sometimes the nature of the cathodes is also uncertain. Practically, however, it is a simple matter to determine a composite of the resultant potentials and their change with time. These time-potential measurements indicate whether the process is anodically or cathodically controlled and in some cases furnish information as to the rate at which it is proceeding, experimental facts which are of value in predicting corrodibility. A recording potentiometer is of considerable assistance in this connection.

Figure 5 illustrates schematically the correlation between these time-potential relationships and the anodic and cathodic polarizations which determine their positions. It will be seen that the potential of iron in a solution of potassium sulfate (represented by the lower solid curve) is mainly determined by the anodic potential of iron in the solution, the cathodic areas being polarized. When potassium chromate is added to the solution the resultant potential of iron is shifted markedly in the cathodic direction, the position being determined by anodic polarization. The actual values of the potential of iron in these cases are of the same order as that of iron alloyed and rendered passive by the addition of chromium and nickel.[24]

In a solution containing hydrogen peroxide, iron is passive even in the acid range as shown in Fig. 6. The abrupt cathodic shift in the potential of iron in the region of pH 6.5–6.8 also shown in Fig. 6 is due evidently to a film which affects both anodic and cathodic areas and which judged from this position would be expected to be less protective than the more pronouncedly passive films (indicated by

their cathodic positions) produced by hydrogen peroxide and chromate ions. A trend of potential in the anodic direction with time, while it may suggest the breakdown of a passive film, does not necessarily indicate the onset of a corrosive attack, for should there also be present substances such as positively charged colloids or other products [25] which tend to raise and maintain hydrogen polarization at the cathodic areas, the metal may suffer little or no attack.

Whether the films which form in corrosion processes are protective in character depends to a considerable extent upon their position or location with reference to the surface of the metal and this in turn
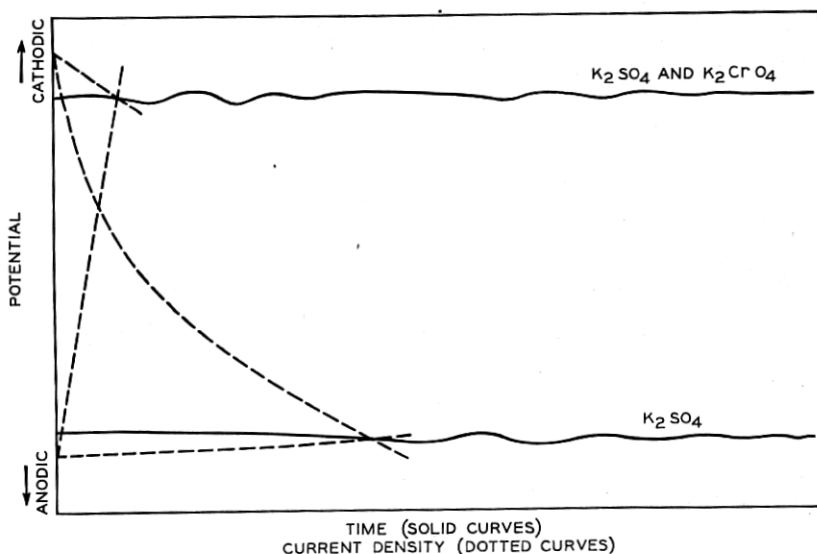

Fig. 5—Time-potential relationship of iron in K_2SO_4 as affected by addition of K_2CrO_4.

depends upon the solubility of the corrosion products in the medium adjacent to the surface. When iron corrodes in the presence of moisture, ferrous ions are produced at anodic areas and hydroxyl ions at cathodic areas, the process continuing until the solubility limit of ferrous hydroxide is attained, whereupon this compound begins to be precipitated as a gelatinous film over the surface of the metal. Increasing the alkalinity of the environment naturally represses the solubility of this compound, precipitating it with less solution of iron. In the absence of oxygen the ferrous hydroxide film tends to inhibit corrosion by maintaining hydrogen polarization. When, on the other hand, oxygen is accessible to the system, ferrous ions are oxidized with the result that ferric hydroxide being less soluble than ferrous
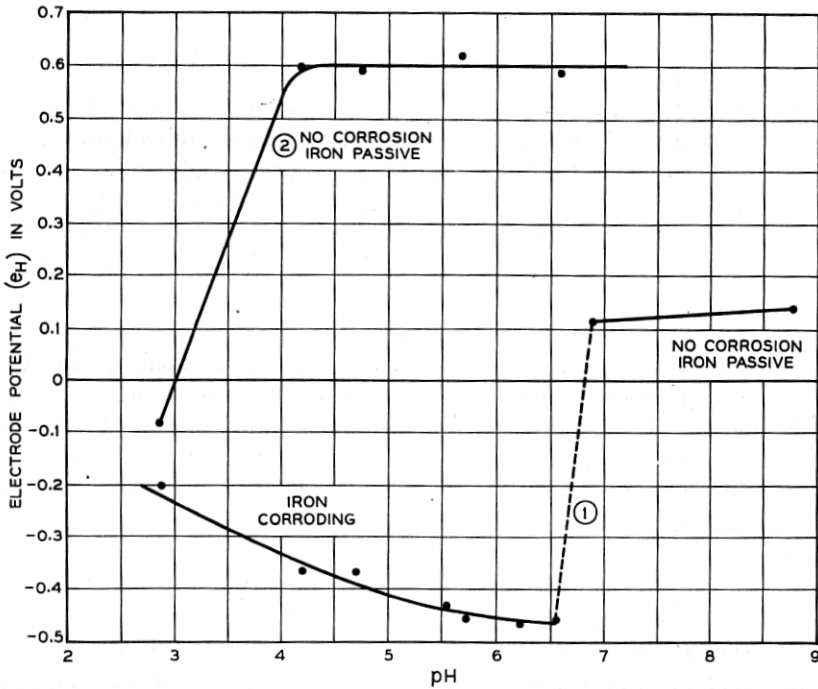
Fig. 6—Effect of acidity and of hydrogen peroxide on the equilibrium potential of iron in buffer solutions of varying acidity.
1. Potential of iron in tenth normal solutions of sodium acetate-acetic acid solutions.
2. Potential of iron in tenth normal solutions of sodium acetate-acetic acid solutions + 0.6 per cent hydrogen peroxide.

hydroxide is precipitated and forms a more or less porous rust film at an appreciable distance from the metal surface. Owing to the mildly amphoteric nature of iron there may exist, especially under alkaline conditions or higher temperatures a considerable concentration of ferrite (FeO_2') ions which, upon reacting with ferrous ions, may precipitate ferrous ferrite (Fe_3O_4) or black magnetic oxide of iron which, also being precipitated in a somewhat granular form at some distance from the surface of the metal, is non-protective. In contrast to these examples is the highly protective film of silicate which presumably forms upon lead and lead rich alloys when immersed in water or soil solutions containing as little as ten parts per million of silicate. As is well known, distilled water is corrosive to these metallic materials. Were it not for this fortunate effect of silicates upon lead it is doubtful that it or its alloys could be used for cable sheathing in the present type of underground construction which permits exposure to soil and surface waters at times.

Studies have shown that the points of failure of air-formed films on iron and steel surfaces indicated by the initial appearance of anodic or rust spots depends upon the previous history of the specimen and upon the medium in which the test is conducted.[26]   For example, an increase in time of pre-exposure to oxygen or exposure to higher temperatures decreases the number of initial anodes, while increasing the chloride content of the medium or the presence of sulfide on the metal surface [27] increases them.   Whether corrosion continues at the points of initial attack often depends upon the self-healing ability of the film, that is, upon plugging the fissures or pores in the film with corrosion products.

Various methods have been considered for the determination of the quality of protective films.   In the case of aluminum and its alloys the amount of leakage current which may pass through anodically formed films throws some light upon resistance to corrosion.   Another promising method applied to iron steel and alloy steels has been to determine by potential measurement the amount of chloride required to destroy passive films formed in water or chromate solutions.[28]

The rate of film formation is in a sense a measure of the activity of a metal surface, that is, a measure of the rate at which a metal might corrode in a homogeneous environment in the absence of film forming constituents.   For example, it will be seen in Fig. 7 that the potential
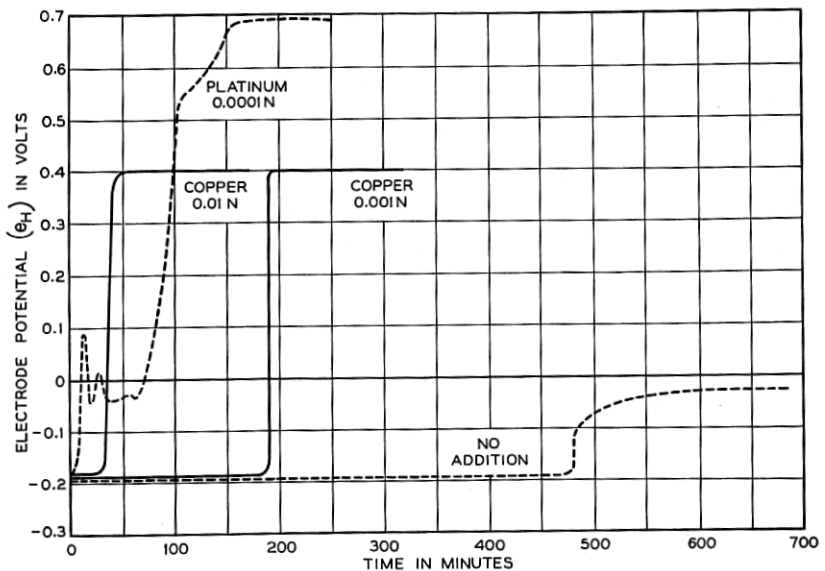

Fig. 7—Effect of traces of copper and platinum on the potential of lead in 0.1 N H_2SO_4.

of lead in tenth normal sulfuric acid breaks rather abruptly after about 500 minutes to the potential of a gas electrode. Apparently the anodic areas become progressively covered with a film or sulfate until substantially the entire surface is passive. Upon the introduction of a drop of thousandth normal copper sulfate, the sulfation of a similar lead specimen is consumated in about 200 minutes at the end of which time the potential breaks to that of the cathodic areas of copper which have been formed by replacement deposition. A still higher concentration of copper brings about sulfation still more rapidly and when the solution is contaminated with platinum a break to the potential of platinum occurs after a still shorter period. In the same manner, the relative corrodibilities of leads of various purities and certain lead alloys [29] has been compared.

The foregoing discussion of the application of electrochemical methods to corrosion investigations outlines techniques by means of which it is possible to get information of the following kind. By the position of the potential of a metal against its environment and the trend of this potential with time it is possible to determine whether the corrosion process is controlled by reactions occurring at the anodic areas, the cathodic areas or both, that is, whether there is a tendency toward passivity, inhibition or progressive attack. Measurements of film stability whether in terms of the leakage current which may be passed through the film, or in terms of the amount of film-forming material (such as chromates) required to produce passivity or the amount of film destroying material (chlorides) required to render the metal active, furnish information as to the quality of corrosion resistant films. Finally measurements of the rate at which a film forms on a metal when placed in a film-forming environment also throws light upon the relative surface reactivity of the metal. Such information is of assistance in determining the rates of corrosion in homogeneous corrosive environments or the rate of passivation in film-forming environments. It is evident in all of these cases that the interpretation of the experimental data which are obtained and the application of the findings to practical corrosion problems is considerably facilitated by a chemical knowledge of the environments in which metals are used as well as the composition and physical state or structure of the metallic material. With such measurements and such knowledge it is possible to predict corrosion behavior and to obtain an understanding of corrosion problems usually not possible by ordinary empirical corrosion tests.

To summarize, the process of corrosion may be one of direct combination of a metal and a non-metal or it may be one in which hydrogen

or another metal is displaced from the medium at the surface of the metal. In either case reaction products appear and usually exert a controlling influence upon the progress of attack. In the replacement type of corrosion process, in which the attack occurs by means of the operation of small galvanic couples at the surface of the metal, it is possible to consider separately those influences which affect anode behavior and those involved in cathode behavior. The course of corrosion or resistance to corrosion may be explained in terms of the anode or cathode control of the process. It is apparent then that a knowledge of both the composition and condition of a metal surface and of the surrounding environment is requisite to an understanding of corrosion problems.

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