INFLUENCE OF THE SUPRAMOLECULAR MARINE ENVIRONMENT ON PITTING CORROSION

by
Denton B. Harris, Bob M. Gallaway and John B. Herbich
Ocean Engineering Program

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ABSTRACT

A mechanism is proposed for the process of corrosion pit nucleation in the marine environment. Rupture of the passive film is described in terms of its sensitivity to attack by negatively hydrated ions. A corollary is suggested which describes the inhibiting effect of various positively hydrated ions. The role of marine microorganisms is discussed as it relates to those environmental modifications that may contribute to pit nucleation.

PREFACE

The study described in this report was conducted as part of the research program in Coastal, Hydraulic and Ocean Engineering at Texas A&M University.

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CHAPTER I

INTRODUCTION

The oceans of the earth consist of a moderately concentrated aqueous electrolytic solution containing a staggering variety of ions and living organisms. Depending upon one's frame of reference, one may consider the ocean to be an environment of change or one of constancy. From the viewpoint of the kinetics of inorganic reactions, the temperature variations of the oceans, both in time and place, are small. Yet from the point of view of a particular species immersed in the ocean, the 25°C to 0°C range of temperature may present a problem of insurmountable magnitude. The concentrations of dissolved substances or second phase substances, when averaged over eons of time, are remarkably constant. However, seasonal variations or variations from one location to another (vertically or laterally) may be of considerable significance in electrochemical and biochemical processes.

There are several aspects of the environment which relate directly to the problem at hand and will be discussed in detail. It should be kept in mind that the ocean is a system, and that no aspect of the ocean can be treated completely and at the same time independently.

We are concerned generally with the effect of ion concentration and distribution on the process of metallic corrosion, but more particularly with the role of halogen ions in the nucleation of corrosion pits. It is necessary, therefore, to set the scene from both the physicochemical and biochemical viewpoints.

Our basic problem is one of understanding the action at an interface. To this end, we must consider the physical, biological and chemical parameters, not only as they prevail in the mass, but as they may be altered at the interface. We must consider the structure of water, the diffusion of electrolytic and non-electrolytic dissolved and second phase material, the respiration and nutrition of protista, and the structure and stability of passivation films.

CHAPTER II

SURFACES AND THE ENVIRONMENT

Metallic surfaces in a vacuum are virtually stable. Only when the surface is exposed to the biosphere do we observe the onset of instability. The envelope of the biosphere includes those reaches of the terrestrial environment which are responsive to the presence of the biochemical process. The oxygen concentration in the atmosphere, the hydrosphere and the lithosphere is directly related to the biochemical process, as is the carbon dioxide distribution. The carbonate cycle is responsible for the buffering of the seas. Any consideration of the instability of metallic surfaces is incomplete if the influence of the life processes is ignored.

The action at a metallic surface in contact with the biosphere may be studied via the following routes: One may seek to explain the action in terms of the chemical process, the electrochemical process or the biochemical process, or one may choose to study the action as a coupling of several identifiable mechanisms which historically have been considered to be the province of independent disciplines. The second route has, in the case of corrosion, received very limited attention. The study given to the chemical and electrochemical processes by investigators over the last half century may be justified by the results that have been achieved in the development of new, more stable materials as well as by protective systems that have been devised for the less stable materials. The interest shown by investigators in the biochemical process has been limited, perhaps, by the seemingly narrower sphere of application offered by readily identifiable evidence of the direct action of an organism.

If one takes the more general overview that all of the processes are indivisibly linked, it may be shown that virtually all corrosion in the "natural" environment is influenced by the presence of biota. The line of action may be more or less direct, depending upon the particular situation; however, the line of action does exist, and if unbroken will result in continued instability and corrosion. The best one can hope for is to retard or delay the action or to loosen the couplings along the line of action in the fight against corrosion.

These several processes are linked by the inorganic matter of the environment. The circulation of the atmosphere and hydrosphere as defined by the principle of planetary fluid mechanics couple the biochemical, electrochemical and dry chemical processes. The coupling may be achieved by diffusion mechanisms independent of planetary circulation. However, as one observes the coupling on an ever-decreasing scale, it becomes increasingly difficult, for example, to distinguish between transport via the diffusion mechanism from transport via microturbulence which resides at the interface between planetary circulation and the thermal state of the environment.

It is this region of action, i.e. the redistribution of the constituents of the environment on a scale smaller than the organism producing those constituents that affect corrosion, yet larger than the species of molecule involved in the chemistry of the corrosion reaction, that has drawn the least attention from theoreticians as well as experimentalists. This situation is understandable, since one is faced not only with difficult experimental techniques, but also with incomplete, if not questionable, theories relating to initial action in the destabilization of passive films. One also is confounded by incomplete theories of mass transport in the boundary layer, and by little understood changes in the immediate environment of biota resulting from their metabolism and respiration as well as charge transport within these organisms. It is conceivable that, by systematic study of the various contributing processes, one might identify those aspects of each process that when interlocked would provide the logical pathway for interaction between the biochemistry, physical chemistry and electrochemistry of corrosion.

The objective of this study is to advance the level of understanding of the physicochemical process inherent in the nucleation of corrosion pits in passivating surfaces exposed to sea water. The thermodynamics and kinetics of electrode reactions will be explored, theories related to the formation and structure of passive films will be analyzed, the composition and structure of sea water will be studied and finally the effect of microbial life will be considered. A theory of pit nucleation will be suggested based upon the best evidence, from all areas, that can be brought to bear upon the problem.

CHAPTER III

THE ELECTRODE

The interface between a metal and a vacuum is negatively charged with respect to the interior of the metal. This surface potential establishes the affinity of the metal for its electrons. Should the interface be between the metal and some other atmosphere, the potential may change. It is also observed that each metal has a characteristic potential. If two dissimilar metals are joined, the metal with the higher affinity for electrons will gather electrons from the metal of lower affinity. The current will flow until the contact potential is equal to the difference between surface potentials of the individual metals (1).

A metal immersed in an electrically conducting solution will undergo a change in its surface potential from that which it exhibits when exposed to a vacuum. The change in potential is referred to as the electrode potential. The fact of the change in potential, as in the case of two metals in contact, is direct evidence of the transfer of charge between metal and electrolyte. In the absence of any other action, a net transfer would proceed until the reaction potential is stabilized. At this point there is no net transfer of charge, but rather a dynamic reversible equilibrium between charge carriers leaving the metallic surface for the solution and those leaving the solution and being redeposited on the metal surface.

There is no direct method for experimentally determining the absolute electrode potential at the surface of a metal in an electrolyte. Nor can we measure the absolute electrode potential difference that results from the exchange of charge between metal and electrolyte. Such a system, i.e. a metal surface in contact with an electrolyte, is termed a "half-cell". Relative electrode potentials are usually reported relative to the Standard Hydrogen Electrode (SHE), which is assumed to be at zero volts. A surface in dynamic reversible equilibrium is characterized by an exchange current density as well as its electrode potential. The exchange current represents the balanced two-way flow of charge across the metal-electrolyte interface. The fact of the exchange current has been verified by radioactive isotope tracer techniques. If a single species of charge carrier is involved in the exchange current, the metal is referred to as an equilibrium electrode, or Type 1; if more than one species of charge carrier is involved, the electrode is nonequilibrium, or Type 2 (2).

A Type 1 electrode potential is proportional to the change in free energy of the electrode reaction, and hence can be computed from thermodynamic data. The Type 2 electrodes may or may not reach a steady state of electrode potential, depending upon the nature of the particular reaction system. In any event, the potential does not characterize the equilibrium state and is therefore termed nonequilibrium or irreversible. In the case of a steady-state Type 2 potential, one may not assume nil mass transport since the charge carriers involved in the exchange current may differ depending upon the sense of flow, i.e. from electrode to electrolyte or from electrolyte to electrode. The flow of positive current from the electrode to electrolyte or negative current from electrolyte to electrode is termed the oxidation, or anodic, reaction, and the counter current is termed the reduction, or cathodic, reaction. The anodic reaction may involve the oxidation of metal atoms ($M \rightarrow M^{++}$), hydrogen atoms ($H \rightarrow H^{+}$) or oxygen ($O^{--} \rightarrow O$) or one or more of a variety of other possibilities, while the cathodic reaction may be the reduction of metal ions ($M^{+++} \rightarrow M^{++}$, $M^{+} \rightarrow M$), protons ($H^{+} \rightarrow H$) or oxygen atoms ($O \rightarrow O^{--}$). It is obvious that for a Type 2 electrode the system $M \rightarrow M^{+}$ and $H^{+} \rightarrow H$ for the anodic and cathodic reactions, respectively, may result in balanced charge transport but may not result in balanced mass transport.

The anodic and cathodic processes may take place intimately over a metal surface or for various reasons may be separated in space even to the extent of occurring on the surface of different metals. The degree of separation forms one basis for the categorization of the corrosion process. Intimate mixing of the reactions is called general corrosion; corrosion at isolated locations on a single metal may be called pitting or crevice corrosion, and when the reactions take place on different metal surfaces we have galvanic corrosion. Other categories exist based on other processes.

As has been noted, the static potential of a Type 1 electrode cannot be measured absolutely. It must be referenced to an agreed-upon standard. The reaction $H \leftrightarrows H^{+} + e$ at a temperature of 25°C and pH equal to zero when the electrolyte is saturated with H is that standard (SHE). The open circuit potential of an active surface under standard conditions and in contact with its own ions at unit concentration and referenced to the Standard Hydrogen Electrode (SHE) forms the basis of the electromotive series.

CHAPTER IV

ELECTROCHEMICAL KINETICS

The Nernst equation expresses the potential of a cell in terms of the temperature of the reaction and the activities of the reactants and products of the cell (3).

$$E = E_o - \frac{RT}{nF} \ln \frac{a_B^d \cdot a_d^c \cdot \ldots}{a_z^z \cdot a_Y^d \cdot \ldots} \qquad [IV-1]$$

In the equation E_o is the potential of the surface at standard conditions and where the activities are unity. E is the potential when the absolute temperature is T and the activity of product of molality b is a_B and of activity of reactant of molality z is a_z. R is the gas constant, n is the chemical equivalents and F is the Faraday. The activity a_B, for instance, is one of the following: the molality b multiplied by the activity coefficient γ, the pressure in atmospheres of a gas phase or unity for solids.

From this thermodynamic relationship, one may develop the expressions for the pH and pressure dependence of both the reversible hydrogen electrode and the reversible oxygen electrode. They are, respectively,

$$E_{H_2} = 0 - \frac{RT}{2F} \ln \frac{(a_{H^+})^2}{p_{H_2}} \qquad [IV-2]$$

$$E_{O_2} = 1.23 - \frac{RT}{F} \ln \frac{(P_{O_2})^{1/2}}{(a_{H^+})^2} \qquad [IV-3]$$

On the supramolecular scale of action, one must also consider the occurrence and action of potentials resulting from the junction of liquids of different composition and/or concentration. Such potentials arise as a result of the independence of mobility and charge. A charge carrier may be driven by a concentration gradient against a potential gradient until equilibrium is achieved and the liquid junction potential is achieved. Similar and related active transport occurs in various biochemical processes, which will be examined in a later chapter.

Thus far, this chapter has been concerned with the prediction of thermodynamic equilibria. From the careful application of the Nernst equation, one can predict the potential difference or reaction tendency between anode and cathode in terms of various properties of the surfaces and the environment. Of special concern to the engineer are the kinetics of the nonequilibrium reaction, or more precisely the corrosion rate of a particular surface in a particular environment. Since the mass flow is proportional to the current flow, and the current flow in turn is controlled not only by the potential but also by the resistance of the circuit, it becomes important to evaluate the occurrence and nature of the various resistive elements.

Impediments to the transport of charge within the reaction system may result from some combination of three resistive mechanisms. First, the flow of charge may be impeded by some element of the circuit of particularly low conductance. This IR drop or potential change due to the resistance in the circuit may be a function of the geometry of the corrosion cell, the conductivity of the medium, and the temperature. Second, the flow of charge may be impeded by the change in concentration of charge carriers in the vicinity of the electrodes due to the oxidation or reduction reaction. This potential drop, termed concentration polarization, is a function of the current density and the nature of the charge carrier and the conducting medium. Third, the flow may be impeded by one or more steps in the reaction that require a high energy of activation. Activation polarization, or overvoltage, is the term used to describe this potential drop, which is a function of the current density as well as the nature of the reaction.

The IR drop or change in potential due to resistance may be expressed as follows:

$$\Delta E_R = i\frac{P}{K} \qquad [IV\text{-}4]$$

where ΔE_R is the resistive potential drop, i is current density, P is some geometric parameter and K is the conductivity of the medium.

The concentration polarization, ΔE_c, is given by the following equation:

$$\Delta E_c = -\frac{RT}{nF}\,\ell n\,\frac{i_L}{i_L - i} \qquad [IV\text{-}5]$$

where i_L is a limiting current density determined on the basis of diffusion. From Fick's law, the limiting current density is given by:

$$i_L = \frac{D_n F}{\ell t}\,c \qquad [IV\text{-}5a]$$

Here c is concentration of the diffusing species in the medium, ℓ is the thickness of the Nernst diffusion layer, t is the transference number and D is the diffusion coefficient. The transference number for electrolytes containing many ions approaches unity. Normal values range as $0.2 < t < 0.8$. It is assumed here that the concentration at the reacting surface is very small with respect to the concentration c of the medium.

Activation polarization ΔE_A, is given by the Tafel equation:

$$\Delta E_A = \beta \log \frac{i}{i_o} \qquad [IV\text{-}6]$$

where β is the Tafel slope. It is a function of the given charge transfer reaction at the given interface and the exchange current density. In this equation, β is usually close to 0.1 volts for reactions of interest to the corrosion engineer and i_o is the exchange current density (4).

CHAPTER V

PASSIVITY

The corrosion reaction is driven by the potential difference between anode and cathode and is controlled by polarization. The idealized relationship may be shown graphically by the Evans diagram in the following way (5):

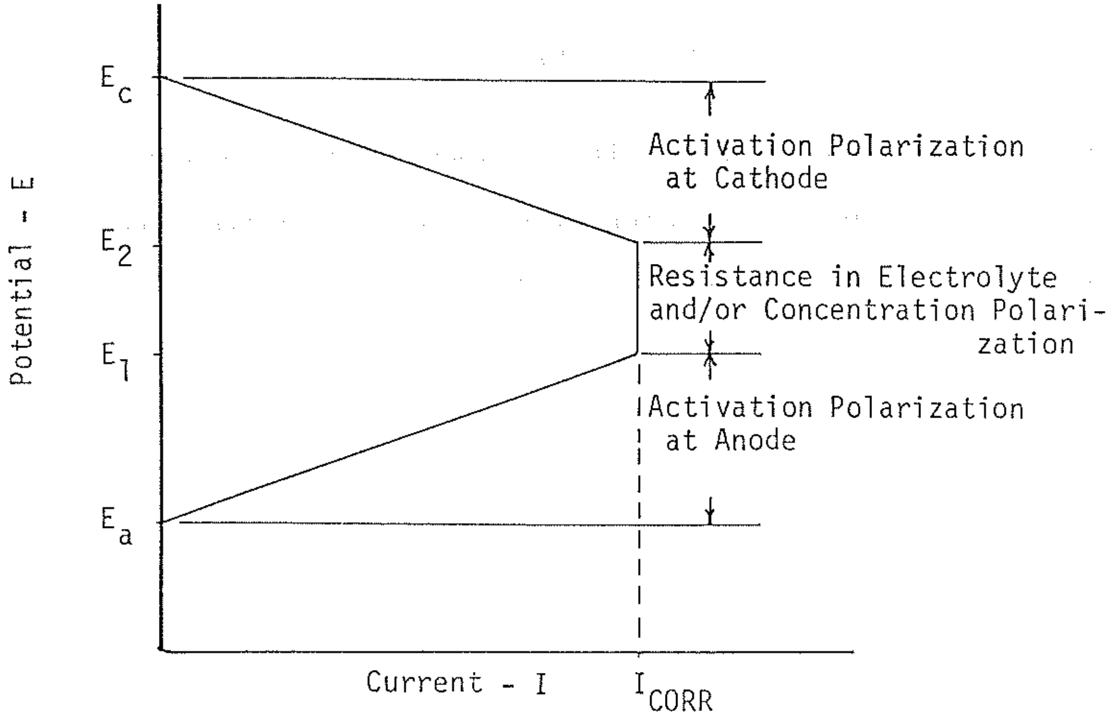

Fig. V-1. Typical polarization diagram.

When polarization occurs only at the cathode, the reaction is said to be cathodically controlled. Similarly, anodic control would exist when only anodic polarization is present. Mixed control is as shown in Fig. V-1. The corrosion current I_{CORR} is as indicated, and in the case of electrolyte resistance the corrosion potential E_{CORR} would have a value between E_1 and E_2, depending upon where in a geometric sense the potential is measured. For electrolytes of high conductivity placed close together, the IR drop may be negligible and E_{CORR} would be a singular value. A singular value also exists in the case of concentration polarization.

The effect of the relative area of anode to cathode is of special concern in establishing the corrosion rate. It is obvious that for steady-state nonequilibrium reactions the anodic and cathodic currents must be equal. However, should the active areas differ, the current density also will differ. A particularly difficult situation exists when a relatively small anodic area is under cathodic control. The result is a high mass transfer or corrosion rate. Equations such as the Stern-Geary (4) equation have been derived for the prediction of corrosion currents from known Tafel constants, limiting current densities and relative areas.

Of singular importance in the control of the corrosion current is the little understood phenomenon of passivity. One can imagine that by the proper application of external potential the anodic or oxidation reaction can be transferred from one surface to another, a process referred to as cathodic protection. If a reverse potential is applied the anodic reaction is accelerated. The unexpected result of such a reverse potential is, for many systems, the establishment of a stable, or passive, state in which the corrosion rate is several orders of magnitude less than for the active state. Forced passivity, as this phenomenon is called, is generally achievable for most metals over a range of potential when exposed to a solution containing its own ions and at controlled pH. Even stranger is the fact that under various conditions some metals and alloys are self-passivating, i.e. they will assume the passive state without an externally applied potential.

The idealized potentiokinetic polarization curve for a passivating electrode at a particular pH and ion concentration might appear as follows:

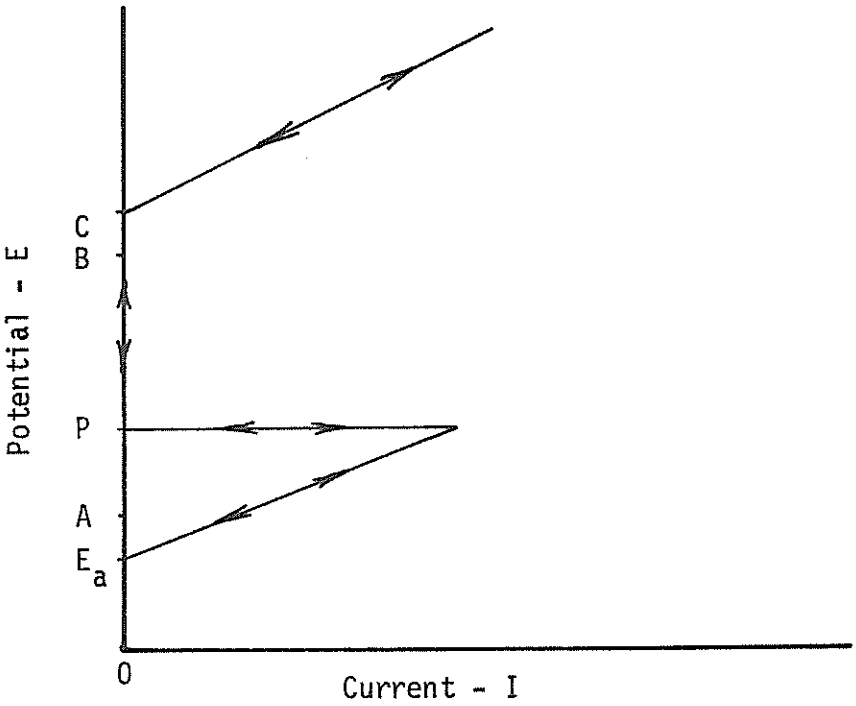

Fig. V-2. Typical potentiokinetic curve for a passivating electrode.

As the diagram suggests, below E_a the surface is stable and immune to corrosion. At potentials between E_a and P and above C, corrosion occurs. Between P and C the surface is passive and resists corrosion. A is the potential of the hydrogen electrode and B is the oxygen electrode, as previously discussed.

The particular case of iron in a solution of its own ions is useful in describing the details of the various reactions. In this example, the concentration of iron ions is held at 10^{-6} moles per liter and the pH at 7. The electrode potential for iron under these conditions is -0.6 volts (SHE), corresponding to E_a in Fig. V-2 (p. 16). Below this potential, iron in solution tends to plate out and any ferric oxide on the electrode is reduced to the metallic state; H^+ is reduced to H_2, and O_2 to water and possibly further to H_2O_2. The electrode is cathodically protected and H_2 is evolved. As the potential is increased to the range between -0.6 and -0.4 V (between E_a and A), Fe is oxidized and hydrogen is reduced. Any ferric oxide on the electrode is reduced to ferrous ions in solution and O_2 is reduced. In this range, iron is corroding in the "normal" or general corrosion mode. Between -0.4 and -0.2 V (A to P in Fig. V-2, p. 16), the iron corrodes without hydrogen reduction and at a potential more positive than that at which -0.2 V passivation occurs. The mechanism of passivation, for which there are several theories, will be discussed later. The region -0.2 to +0.8 V is characterized by the possibility of spontaneous passivation without external energy if the solution is moderately oxidizing. Above +0.8 V (SHE), only oxidizing reactions occur in this system. The principle oxidization is $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$.

The potential-pH or Pourbaix diagram is constructed from potentiokinetic data at various pH values and ultimately for various concentrations of various ions. The Pourbaix diagram for iron is shown in Fig. V-3 (6-12).

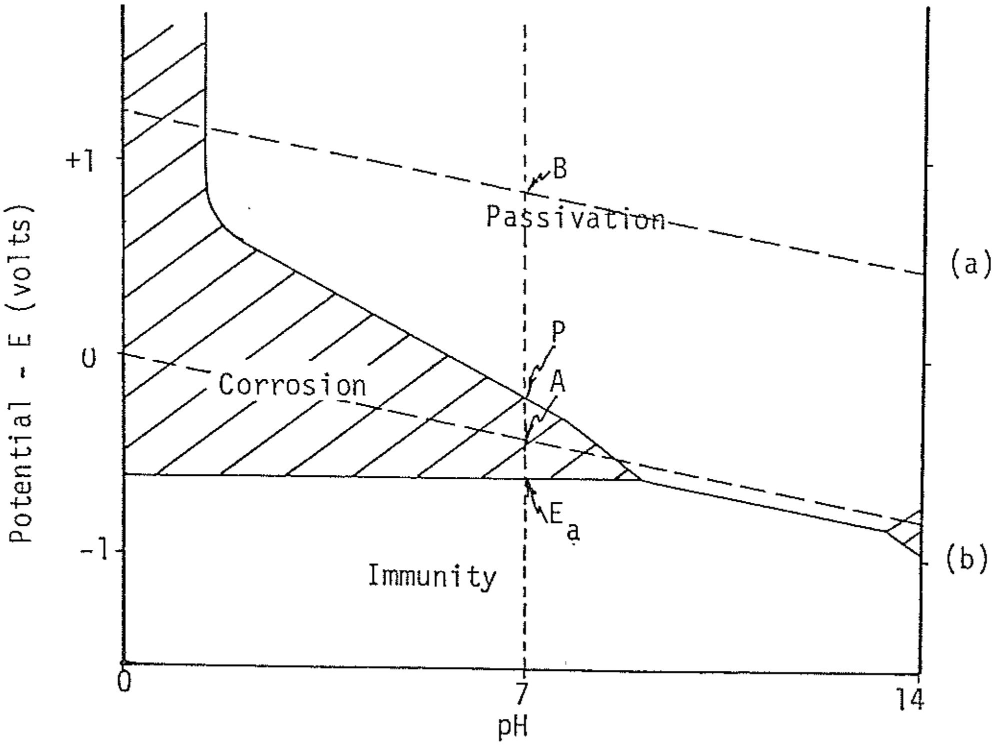

Fig. V-3. Pourbaix diagram for iron.

In this figure, the vertical dotted line is from Fig. V-2 (p. 16) for nil current. The Pourbaix diagram, therefore, gives a summary of the thermodynamic state of the system. Note that in the region of pH 7 small changes in pH will result in changes of the potential of point P, the active-passive transition. The situation becomes more complex with the addition of chloride ions to the electrolyte. The effect of chloride addition is to alter the potentiokinetic responses of the system in the previously passive region, as shown in Fig. V-4.

For iron passivated in a chloride-free environment, the poten-

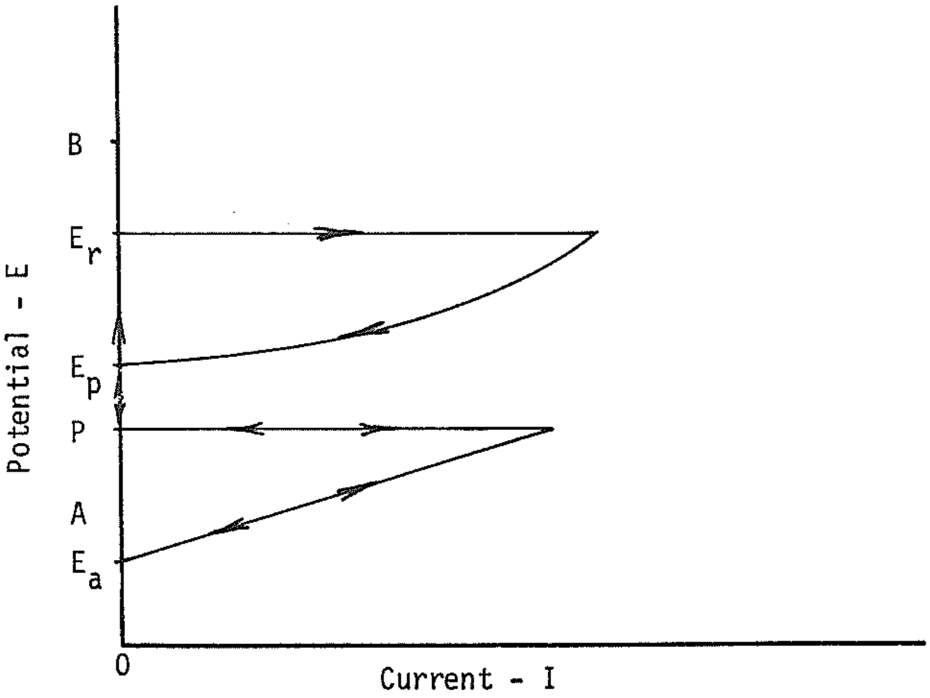

Fig. V-4. Typical potentiokinetic curve for a passivating electrode with chloride ions present.

tiokinetic curve in the presence of chloride ions will be the same as in Fig. V-2 (p. 16) until P is reached. As the potential is raised above P the presence of the chloride ions is felt. At E_R, the rupture potential, local failure of the passive film occurs and corrosion pits result. Subsequent decrease of the potential reduces the corrosion current, and at E_p, the protection potential, the pits become inactive. In this condition, the surface is stable between E_p and P. Between E_p and E_R, the surface is stable if no pits are present and unstable if pits are present. If E_R is more positive than B, pitting is rare even when the protection potential is more negative than B.

The potential range between P and E_p is termed a zone of perfect passivation, whereas between E_p and E_R there exists imperfect passivation, since corrosion will occur if pits are present.

The general form of the Pourbaix diagram for iron in chloride, including the zones of passivation, appears as follows

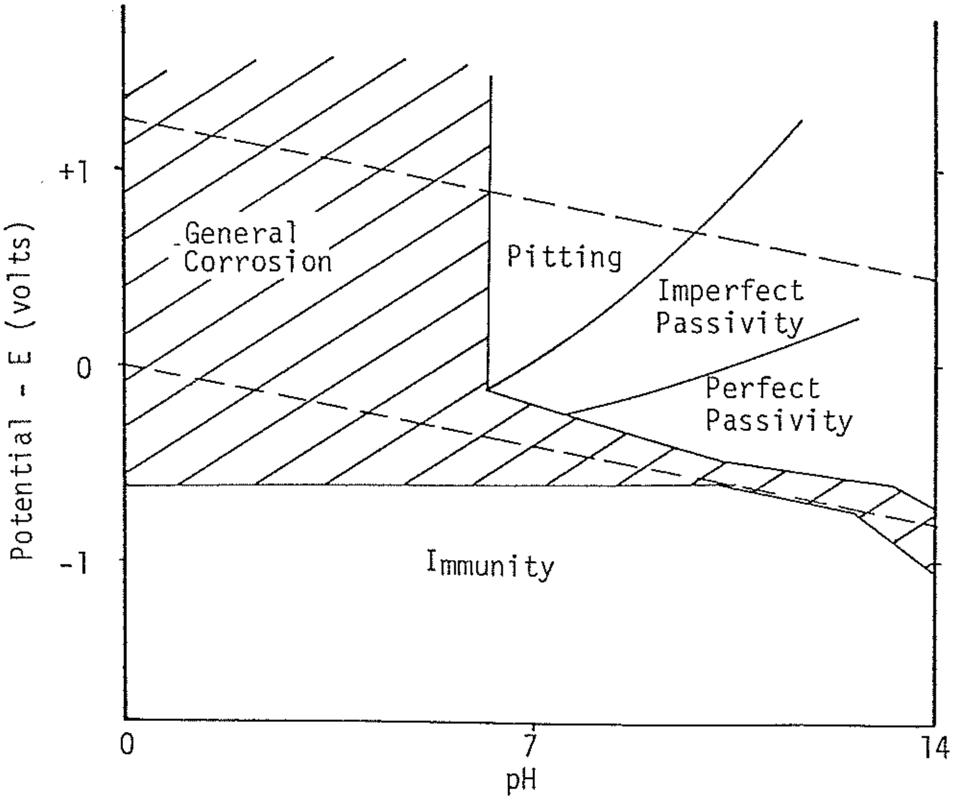

Fig. V-5. Pourbaix diagram for iron with chloride ions present.

Potential-pH diagrams for AISI 410 and AISI 304 in 0.1 molar Cl^- are shown in Figs. V-6 and V-7, respectively. It should be noted that these data are unconfirmed but may be considered representative (11).

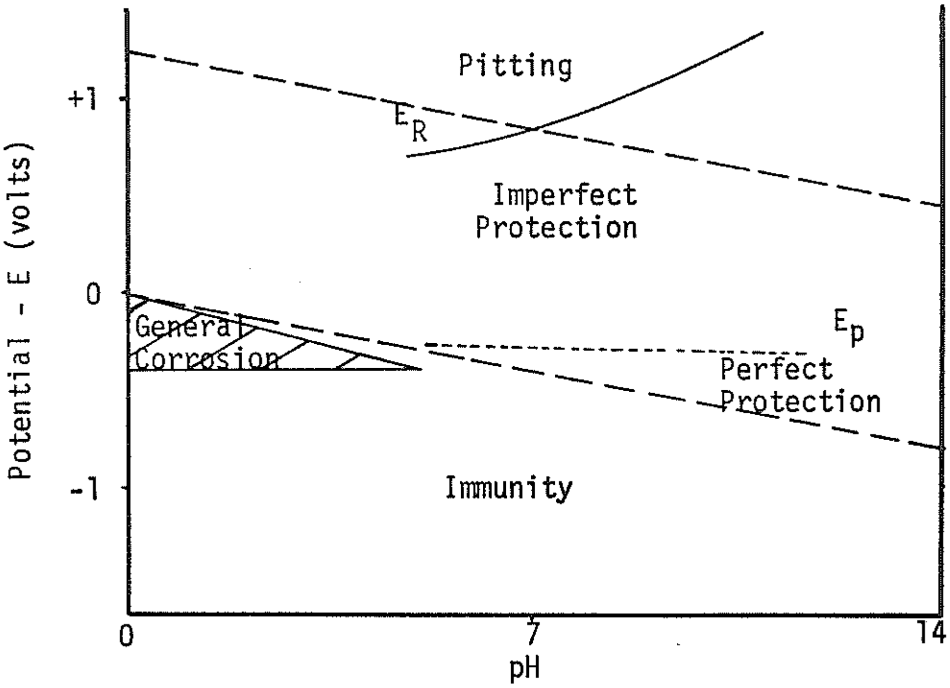

Fig. V-6. Pourbaix diagram for AISI 304 in 0.1 M Cl^-.

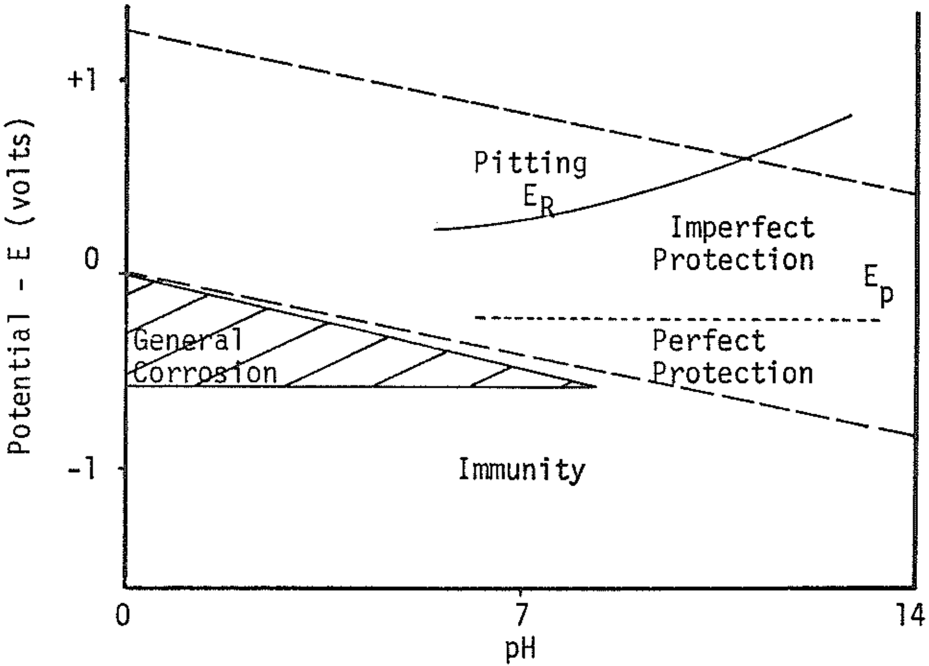

Fig. V-7. Pourbaix diagram for AISI 410 in 0.1 M Cl^-.

Several theories have been proposed for the mechanism of passivation. The theory in keeping with the weight of evidence is the adsorption theory, which proposes a chemisorbed film of oxygen which, in replacing the normally adsorbed layer of water molecules, inhibits the hydration of metal ions at the anode. The observed spontaneous passivation of the transition metals supports this theory in that their unpaired d electrons contribute to a mixed homopolar-heteropolar bond of higher energy than that which might occur with a more completely heteropolar bond structure (4). Conditions may exist which favor the formation of metal oxide films which function as low conductivity barriers in addition to or as replacements for the chemisorbed oxygen layer (13). The breakdown of passive iron is observed at 0.6 volt (the Flade potential), a value too high to be identified with any iron-iron oxide equilibrium. Therefore, even though oxides may exist, it would seem that they are imperfect and that chemisorbed oxygen is the primary defense against corrosion of passive iron.

The presence of halogen ions, in particular Cl^-, results in localized destruction of the passive film. The mechanism by which this takes place is imperfectly understood, even when applied to what is assumed to be a perfectly understood passivating mechanism. It appears that, due to subtle variation in the passive film, Cl^- is preferentially adsorbed in competition with oxygen or water, and in the adsorbed state promotes metal dissolution. The potential difference between the active and passive areas varies among the various metal-electrolyte systems, but is in the range of 0.5 volts.

CHAPTER VI

IONIC TRANSPORT

Water molecules and ions in solution move on the macro scale by the accepted means of oceanic transport, tides, currents, welling, etc., and on the micro scale by thermal and concentration diffusion, turbulent diffusion, convective-diffusive transport and ion drift resulting from field effects. Macro scale motion homogenizes the oceans, as noted previously in Chapter I and are of concern to the corrosion engineer in predicting rates from one construction site to another. Micro transport phenomena, however, is central to an understanding of inhomogeneous nucleation of corrosion. The following approach to diffusion begins with self-diffusion and Fick's first law (3).

Self-diffusion involves no net transport in any direction. It is thermally activated, and is a form of random walk without the influence of field effects or concentration gradients. In the presence of a gradient $\frac{\Delta c}{\Delta x}$ the flux J is given by Fick's first law:

$$J = -D \frac{\Delta c}{\Delta x} \qquad \text{[VI-1]}$$

The diffusion coefficient D is characteristic of the system. The values for D_o (the self-diffusion coefficient) of pure water at 5°, 10° and 25°C have been measured by tracer techniques to be 1.43, 1.68, and 2.57 X 10^{-5} cm^2/sec (14). Upon electrolyte addition, the self-diffusion coefficient is altered, depending upon the type of ions, to a higher or lower value. NaCl reduces D_o while

KCl increases it. There is, as one observes, inverse but parallel change in viscosity η, i.e. lower D_0, higher η. This is an interesting and not an obvious result. In order to understand this effect, one must consider the effect of structure on diffusion and viscosity (15). The asymmetric water molecule, because of its dipole field, is susceptible to short-range structure. Hydrogen-bonded clusters of water molecules are in a dynamic state of formation and disintegration. The relaxation time for this process has been calculated to be around 10^{-11} sec at 20°C, a time sufficiently long to propose that fluid flow may be considered as via the route of rigid clusters in unassociated water molecules. Increasing the temperature decreases the relaxation time (10^{-12} sec at 40°C), which is consistent with the model having a lower volume fraction of clusters and a lower viscosity. The addition of electrolyte changes viscosity, suggesting a relationship between cluster formation, relaxation time and the nature of the ionic species. Horne has proposed a model for the hydration atmosphere of the sodium ion which calls for a core or electrostricted zone composed of the sodium ion surrounded by a monolayer of water molecules (15). The water dipole orientation is such that the protons form a sphere of positive charge which is the secondary nucleus of the cluster. The structural density decreases as order decreases, moving from the Na^+ core to the free water surrounding the cluster. By observing the relationship between the activation energy for cluster formation and electrolyte concentration, Horne and Birkett were able to estimate the number of water molecules in the structure-enhanced zone of the hydration atmosphere of the sodium ion (16). This model is an elaboration of the Frank-Wen cluster model, which in turn was an improvement over Gurney's co-sphere concept.

Of special interest is the fact that not all electrolyte additions result in higher viscosity. Some result in decreased viscosity, indicating that, in accordance with the correlation with structure enhancement, some electrolytes tend to cause a net breaking of structure (17). In fact, the halogen ions as well as several cations may be considered as structure breakers, in contrast to most of the alkali metal ions, which are structure makers. Mg^{++} is a very strong structure maker. The ratio of the residence time of a water molecule in the immediate vicinity of an ion to the residence time at a considerable distance from the ion is a measure of the effect of the ion on structure, and hence viscosity, Reynolds number and diffusion rates. I^-, Br^-, Cl^-, Cs^+ and K^+ have ratios in the range of 0.58 to 0.65, whereas Na^+, Ca^{++} and Li^+ range from 1.46 to 3.48. Mg^{++} has a ratio of 86.31. From these considerations, the enhancement of self-diffusion of water by addition of KCl becomes understandable, whereas NaCl should decrease self-diffusion and a Mg salt such as $MgSO_4$ should show a considerable reduction in self-diffusion. This, in fact, is in agreement with the experimental observations of Devell (15).

CHAPTER VII

STABILITY OF PASSIVATION

The following is an attempt to define the interaction between those several forces, summarized in previous chapters, that are responsible for the nucleation of the corrosion process.

A fresh metallic surface in vacuum is negatively charged by virtue of the "free" nature of the electrons associated with the metallic bond. The condensation of this field is the source of energy for adsorption on the surface when exposed to pure water. The adsorbed species is the hydrated proton or hydronium ion $H(H_2O)_n^+$. From mobility consideration, the initial adsorption proceeds with ions of low ionic weight followed by those of higher ionic weight. Oxidation of the most energetic atoms on the metal surface proceeds via the reduction of hydronium. At atmospheric pressures, the slow step in proton transfer to the surface, for reduction, results from the high activation energy for conductance by the rotation mode in contrast with the proton flip mode of hydrogen-bonded chains which takes over at high pressure (3). The energy associated with the formation of the hydronium ion, its drift toward the surface, the proton transfer within the ion and its ultimate reduction and diffusion from the surface constitutes a measure of the activation polarization for the cathodic reaction. The metal ion upon liberation from the surface is immediately hydrated and departs the region of the surface at a rate determined by the size and density of its electrostricted zone. Higher temperature and/or pressure reduce the size of the zone, increasing its mobility and promoting a higher diffusion rate.

Depending upon the energy level of the surface, the cathodic reaction may proceed by the reduction of hydronium to the hydroxyl ion. This is expressed as follows:

$$H_3O^+ + 2e \rightarrow H_2 + OH^-(-0.414V\ SHE) \qquad [VII-1]$$

This is in contrast to the single reduction previously mentioned:

$$H_3O^+ + e \rightarrow \frac{1}{2} H_2 + H_2O(0.0\ V\ SHE) \qquad [VII-2]$$

The normally negatively-charged metal surface may be made positive by external electron pumping. The result may be anodic depolarization via the oxidation of hydroxyl ions:

$$4OH^- - 4e \rightarrow 2H_2O + O_2(+0.816\ SHE) \qquad [VII-3]$$

This reaction is most likely paced by the rate of one of the electron capture reactions such as the hydroxyl ion to hydroxyl radical,

$$OH^- - e \rightarrow OH \qquad [VII-4]$$

or the perhydroxyl ion to perhydroxyl radical,

$$HO_2^- - e \rightarrow HO_2 \qquad [VII-5]$$

The limiting current density imposed by concentration control is a factor in this reaction, in contrast to [VII-1] and [VII-2], where the proton mobility is impeded little by the hydronium ion structure.

The behavior of the electrode changes if the water contains dissolved oxygen. The solubility of oxygen in water at standard conditions is of the order 0.001N. This low solubility coupled with a low diffusion coefficient indicates a strong tendency for the oxygen depolarization reactions to be current-limited. An additional factor is the much lower exchange-current density of the oxygen depolarization as compared to hydrogen (10^{-14} amps/cm^2 vs. 10^{-6} amps/cm^2 on an iron electrode at pH = 0) depolarization, which favors the hydrogen depolarization reaction at $pH < 7.5$ even though the potential or thermodynamic driving force for oxygen depolarization is 1.229 V more positive than hydrogen over the entire range of pH. Other cathodic reactions involving oxygen and at pH = 7 are

$$O_2 + 2H_2O + 2e \rightarrow H_2O_2 + 2OH^-(+0.268\ V\ SHE) \qquad [VII\text{-}6]$$

$$O_2 + 2H^+ + 4e \rightarrow 2OH^-(+0.816\ V\ SHE) \qquad [VII\text{-}7]$$

The rate-controlling steps in these reactions are again those involving electron capture rather than transfer (3).

The anodic metal dissolution reaction involves ionic transport and ultimately hydration.

The cathodic metal depolarization reaction involves electron transport and electronation. The passive state is said to exist when an electrode by virtue of some interfacial phenomenon is made inactive under conditions which thermodynamically call for action. The interface between metal and electrolyte is of such a structure as to severely limit one or both reactions mentioned above, i.e.

ionic or electronic transport across the interface. The structure of the interface is the object of much speculation, from a "dry" oxide film on the one hand to adsorbed oxygen on the other. The current adsorption theory suggests that a relatively strong bond may form between the transition metals and oxygen, both having uncoupled electrons. This, in conjunction with the high heat of sublimation of the transition elements, favors adsorption rather than an oxide formation reaction, which involves displacement of the atoms from the lattice sights. A monolayer of oxygen atoms chemisorbed on the surface of the metal followed, according to most theories, by an adsorbed layer of oxygen molecules is the currently proposed structure of the passive layer. It is suggested here that water molecules rather than oxygen molecules are adsorbed on the atomic oxygen. This is consistent with the observations of Okamoto and Shibata, who reported H_2O in passive films on stainless steel, and also the work of Kudo and Yolken, who report the same result for passive iron (18). Flade potentials adjusted for pH as measured on several spontaneously passivating surfaces are in general agreement with the equilibrium potential for the peroxide reaction of equation [VII-6], although little is known of the chemical stability of the adsorbed layer other than the fact that it appears to be much more stable than oxide phases of the same metal. Reaction [VII-6] supports the oxygen monolayer plus water adsorption via the peroxide product of this cathodic reaction. The simultaneous metal ion anodic oxidation product is reduced by the hydroxyl ion product of reaction [VII-6]. The anodic and cathodic reactions are not only simultaneous reactions, they are superimposed spatially as well.

It is well known that halogen ions in the electrolyte contribute to the localized destruction of passivity on most metals and alloys. Several theories have been proposed for the mechanism of this process, and most begin with the supposition that halogen ions are selectively adsorbed as replacements for oxygen atoms. An alternate process involving the structure-enhanced layer of adsorbed water is suggested by the structure-breaking properties of halogen ions. These negatively charged ions tend to coalesce in local areas of higher positive charge associated with geometric and structural irregularities. Their propensity for breaking water structure (negative hydration) results in the de-adsorption of water molecules and exposure of chemisorbed oxygen atoms to direct replacement, as well as stimulation of the relative concentrations of free water near the surface, which is then available for hydration of metal ions from the de-electronation reaction. The corrosion potential for most metals in sea water is relatively independent of the concentrations of its own ions in the electrolyte, indicating that the hydration reaction proceeds at a high rate and in close proximity to the anode surface.

The structure making and breaking properties of various ions, as discussed in a previous chapter, are also of significance in the stabilization of passive films as well as in their destabilization as considered in the above paragraph. Mg^{++}, Ca^{++}, Li^{+} and Na^{+} are structure makers (17). The ratio of the residence times for water molecules near and far from the Ca^{++} ion is 2.16 compared to 1.46

for Na^+, which may account for the observed but little understood fact that calcium compounds are better inhibitors than sodium compounds. The ratio for Mg^{++} is 86.31, indicating very strong forming ability, but its salts form weak electrolytes (incomplete dissociation) and contribute much less, mole for mole, to the inhibiting process. Garrels and Thompson have tabulated the distribution of species in normal sea water (19). Sodium and potassium are 99% free ions; the other 1% is with sulfate, whereas magnesium is only 87% free ion, 11% with sulfate and 1% with bicarbonate. Calcium, another strong structure former, appears as 91% free ion; 8% with sulfate and 1% with bicarbonate.

In the preceding paragraphs the construction and destruction of passivity has been shown to be related to the water structure modifying influence of dissolved ions. There appears to be a firm basis for experimental verification of this proposal by potentiokinetic studies of systems of carefully controlled ionic species.

CHAPTER VIII

BIOCHEMICAL DESTABILIZATION OF PASSIVITY

The ongoing metabolic and respiratory functions of protista of necessity alter the composition of their immediate atmosphere (20). In a previous chapter the alteration of the physical environment was discussed. Changes in pH and in ion concentration were posed, and it may be here stated that these changes have a marked effect on the stability of the passive layer. The proton-rich atmosphere surrounding many bacteria results, according to the chemiosmotic hypothesis, from active transport of electrons across cellular membranes. The energy-rich proton gradient resulting from the active electron transport is said to cause the primary biochemical reaction

$$\text{ADP} + \text{phosphate} \leftrightarrow \text{ATP} + H_2O \qquad [\text{VIII-1}]$$

The casual mechanism is the removal of H_2O by the production of hydronium and hydroxyl ions, since the free energy of the reaction is positive and will proceed to the right only with a coupled reaction involving water removal. The redox potential, since the reaction takes place at a nominal $pH = 7$, is $E = -0.42$ V(HE), and according to Mitchell part of the proton gradient may be replaced by an energetically equivalent potential gradient (21). The combined effect is the lowering of pH and/or potential. Chemolithotrophs may utilize not only hydrogen as electron donors, but also sulfur, divalent iron and nitrogen, resulting in reduced atmospheres and a path for cathodic depolarization.

According to Van Niel, the photosynthetic process in both plants and bacteria may be summarized in the following equation:

$$2H_2D + CO_2 \xleftrightarrow{\text{light}} (CH_2O) + H_2O + 2D \qquad [VIII-2]$$

where H_2D represents the electron or proton donor and D the oxidized form (20). All photosynthetic organisms except bacteria use water as the donor and evolve molecular oxygen. The consumption of CO_2 and in particular the production of O_2 obviously can have an effect on the stability of a passivating layer. A more general form of equation [VIII-2] is

$$H_2D + A \xleftrightarrow{\text{light}} H_2A + D \qquad [VIII-3]$$

D is the electron donor and A is the acceptor. Depending upon the species, the acceptor may be NO_3^-, N_2, H^+ or others. It is clear then that this biochemical process may result in no potential or pH change in the environment, or, in species selective fashion, may promote the anodic or the cathodic depolarization reaction. For the reaction involving water as the electron donor, the electron transfer would proceed at a potential of +0.82 V (HE) at pH = 7 (see equation VII-7]. In any case, the electron flow is in the direction of the system having the more electronegative potential, which from a purely thermodynamic point of view (assuming coupling of the reaction) will promote the corrosion reaction. The biochemically modified atmosphere in the immediate vicinity of a functioning organism is an atmosphere capable of promoting a higher rate of electrochemical activity by virtue of its possible contribution to the depolarization of cathode and anode.

In addition, the modification of the environment by the production of O_2 as well as by alterations in the concentration and balance of ionic species will have an effect on the production and stability of the passivating layer.

From what is known of diffusive and turbulent transport (22) on a scale relevant to the atmosphere of a protista, one would expect gradients of sufficient magnitude to account for induction of the observed inhomogeneous and very localized process of corrosion pit nucleation.

CHAPTER IX

PIT NUCLEATION THEORY

The author's objective, stated at the end of Chapter II and again at the beginning of Chapter VII, is the development of a consistent theory of corrosion pit nucleating in materials exposed to the marine environment. In the previous chapters, the author has discussed various fields of knowledge related to the central question. These discussions are based upon extensive research and amplify, within each field of knowledge, those mechanisms which, when interrelated, form to the author's satisfaction a coherent, consistent and, at the present state of knowledge, a complete theory of corrosion pit nucleation in the marine environment. This theory, as developed in previous chapters, will be summarized here.

The structure of the passive film, as proposed by the author, is consistent with the peroxide depolarization reaction. The strong oxidation potential of the peroxide accounts for the energetics of the film formation. The range of electrochemical potential for which the film is stable is consistent with the potential for the peroxide reaction. The film composition, i.e. chemisorbed oxygen atoms and adsorbed water, also is consistent with the metal-peroxide reaction and, in addition, is confirmed by experimental observation (23).

The destabilization of the passive film by chlorine ions is a thoroughly documented fact (24 - 28). Previous theories have stated simply that the chlorine displaces adsorbed oxygen. The mechanism is not discussed, nor is the roll of inhibitors of corrosion discussed in relation to a destabilization mechanism. The author has suggested that, in fact, the mechanism of film destabilization is based upon the measured negative hydration potential of the chlorine ions and its interaction with the adsorbed water in the passive film (17). Negative hydration decreases the viscosity in the vicinity of the chlorine ion and, projected to the film interface, provides the energy necessary for de-adsorption of the water molecules. The exposed chemisorbed oxygen atoms then are open to direct replacement by the chlorine ions, with the final result that metal ions are displaced from the exposed surface. This is the event of pit nucleation. From this point onward in the electrochemical process, the "normal" mechanisms prevail, i.e. concentration cells, differential area cells etc. (2).

The above process also is consistent with corrosion inhibition phenomena. Some literature in this field theorizes that inhibition results from the adsorption of various positive ions at the interface between the material and the solution. This author suggests that, consistent with hydration theory and the measured positive hydration potential of several inhibitors, destabilization and inhibition are two facets of a single process. Positive hydration increases viscosity at the interface and stabilizes the passive film. This reduces the chance of active ions, such as chlorine, reaching the chemisorbed oxygen.

The above process upholds the speculations of various authors concerning the influence of the geometry and structure of the surface on the pitting mechanism (28 - 30). The compactness of the oxygen monolayer and the superimposed water layer are related to the surface geometry and structure. Areas on which surface metal atoms experience the lowest coordination will obtain the most energetically stable film. Locations with high coordination, such as the re-entrant corner of a step on the surface, will be protected by a lower energy film, which is more prone to attack by active ions and likewise more subject to protection by inhibiting ions.

Environmental factors such as fluid shear stress in the interface, local pH changes and variations in dissolved oxygen concentration resulting from organisms may influence the nucleation process by modifying the boundary layer flow and, this author suggests, by functioning as an electronic conductor in the cathodic depolarization process. The structure of the "bioelectrochemical" cell, providing the rupture potential, then would consist of a stalked bacterium functioning as a cathode, with the anodic area in a stagnation zone at the root of the stalk.

As noted by the author in the above paragraphs, the proposed theory of pit nucleation in the marine environment provides a prediction of behavior that is consistent with observations made and reported to date. However, it appears possible that further substantiation of the theory could result from carefully controlled experiments involving various ions of different hydration potentials. It is this author's intention to conduct such a series of experiments.

GLOSSARY

ADP is the biochemical shorthand for adenosine diphosphate

ATP is the biochemical shorthand for adenosine triphosphate

COORDINATION is the number of equidistant nearest neighbor atoms

FLADE POTENTIAL is the potential at which a passive surface reactivates

POTENTIOKINETIC describes the experimental process by which the current response of a cell is determined during a continuously varying applied potential

POTENTIOSTATIC describes the experimental process by which the equilibrium current response of a cell is determined at a series of fixed potentials

LIST OF SYMBOLS

a	activity
β	Tafel constant
γ	activity coefficient
c	concentration
D	diffusion coefficient
D_o	coefficient of self diffusion
E	potential
E_o	potential at standard conditions
E_a	anode potential
E_c	cathode potential
E_{CORR}	corrosion potential
E_p	protection potential
E_R	rupture potential
F	Faraday constant
I	current
I_{CORR}	corrosion current
i	current density
J	flux
K	conductivity
ℓ	thickness of Nernst layer
M	metal atom or ion
n	chemical equivalents
P	geometric cell parameter
p	pressure

LIST OF SYMBOLS (continued)

pH	potential of hydrogen
R	resistance
SHE	standard hydrogen electrode
T	Kelvin
t	transfer number
V	volts

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