Electrochemical Techniques of Corrosion Control

*H. A. WEBSTER**

Since aqueous corrosion is electrochemical in nature, it is logical that electrochemical techniques can be used in its control. The electrochemical corrosion cell is made up of four essential components: (1) the anode or electrode at which oxidizing processes take place and usually corrosion; (2) the cathode -the electrode surface at which reducing reactions take place and corrosion does not usually occur; (3) the electrolyte—an aqueous solution of ionizable substances; and (4) an electronic conducting path between the anodic and cathodic areas. Whether the metal will corrode or not in specific environments has to do with the thermodynamic stability of the metal and the kinetics of the various processes that take place at the anodic and cathodic sites. Pourbaix has produced diagrams which show domains of immunity, corrosion, and passivity in a plot of solution potential vs pH. Since the equations used in the production of this diagram are thermodynamic equations, interpretation of the diagram shows only the possible, the probable, and the impossible. One could state (Figure 1) that a piece of iron in a solution of pH 7 would not corrode at a potential of -800 mV. Further, Figure 1 predicts that iron would corrode between the potentials of -600 and -200 mV, but gives no information whatsoever about the possible rate of corrosion. If the iron were held above the potential of -200 mV, it is very difficult to predict from the information contained in this diagram whether or not corrosion would occur. As you will see later, it will be possible under certain circumstances to ensure that mild steel and many of the transition metals can be passivated in this range of potentials. Of one thing there is no doubt: if iron can be held at the potentials that would keep the iron within the immunity domain, then corrosion is thermodynamically impossible and this will lead into the first part of this discussion, *cathodic protection.*

Cathodic Protection

Cathodic protection is achieved by artificially depressing the potential of a metal such that for the condition of its environment it is held in the immunity domain of a Pourbaix diagram. There are many other definitions of cathodic protection some of which will be enlarged upon later.

Polarization is an important concept when one considers the practical application of electrochemical techniques in corrosion control. In the case of cathodic protection, we are interested in changing the potential of a metal surface by the application of an external current source such that current passes from the electrolyte to the metal surface. Any change of potential at the surface of the metal due to current flow produced either by natural corrosion currents or externally applied cathodic protection
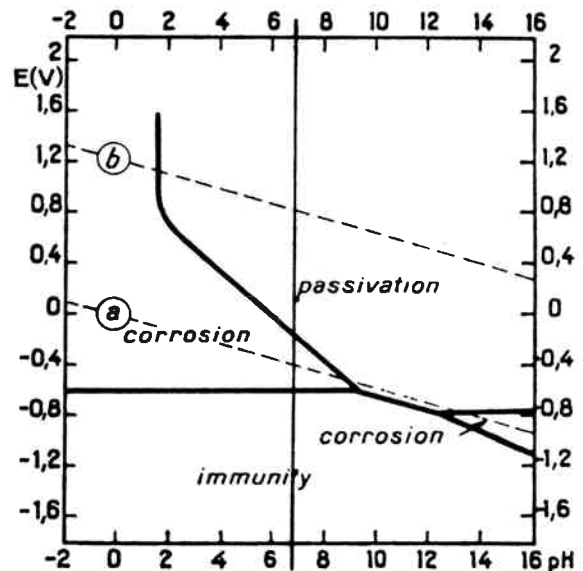

FIGURE 1 — Potential-pH diagram.

currents is referred to as polarization. By means of a very useful instrument called the potentiostat, it is possible to control the potentials of a metallic specimen in an electrolyte and to record the current required to achieve steady state conditions at each potential setting. It is therefore possible to produce polarization curves for anodic and cathodic processes. A typical plot of such a curve is shown in Figure 2. Here essentially we have a straight line relationship between the specimen potential and the log of the current density that is required to produce it. The curved portions at either end of this curve are due to certain activation and concentration effects which will be beyond the scope of this practical discussion. These curves can be idealized by a straight line as has been done by Professor Evans of Cambridge University. These idealized polarization diagrams are known as Evans' Diagrams and are very useful in explaining some of the practical limitations of the economic application of cathodic protection.

Figure 3 shows an anodic and cathodic polarization curve plotted on the same diagram, and in highly conductive solutions such as sea water they nearly meet, and the ordinate at their point of intersection is known as the corrosion potential and the abscissa reflects the corrosion current that flows in this equilibrium state. On this particular diagram you will note that the slopes of the anodic and cathodic polarization curves are numerically the same although of opposite sign. Under these circumstances, the corrosion process is said to be under mixed control. Where cathodic polarization is slight, as in the case of metals dissolving in strongly acid solutions, then the

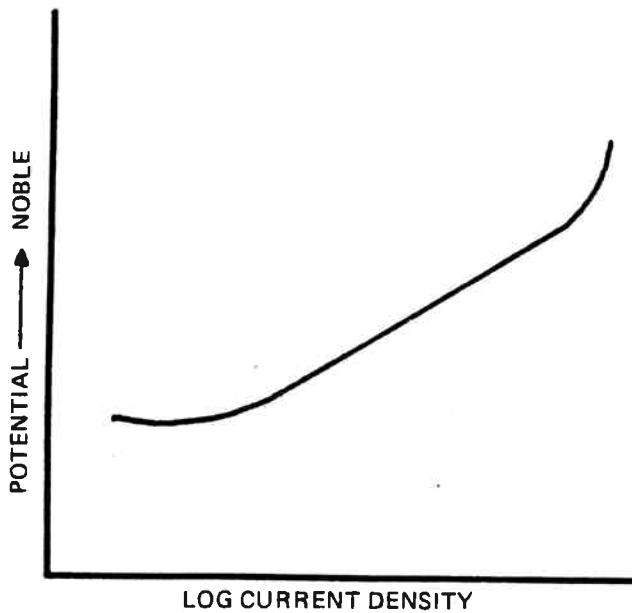*Corrosion Service Co., Ltd., Toronto, Ontario, Canada.
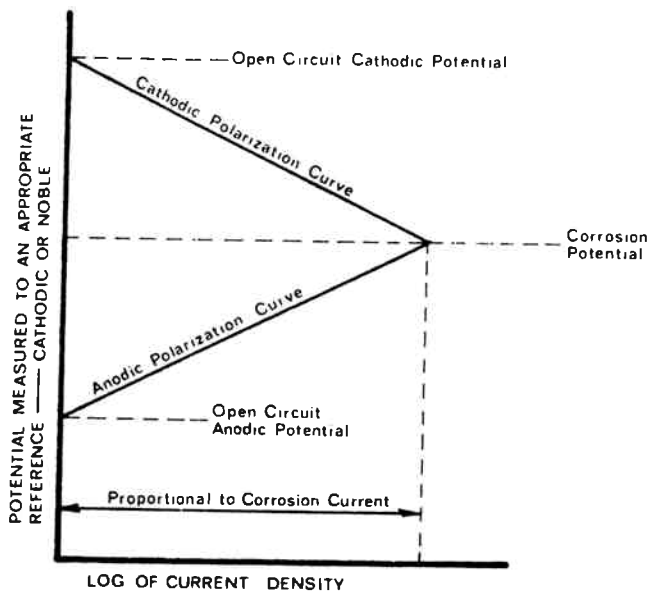
FIGURE 2 — Anodic polarization curve.

FIGURE 4 — Evans' diagram for system corroding under anodic control.

FIGURE 3 — Evans' diagram.
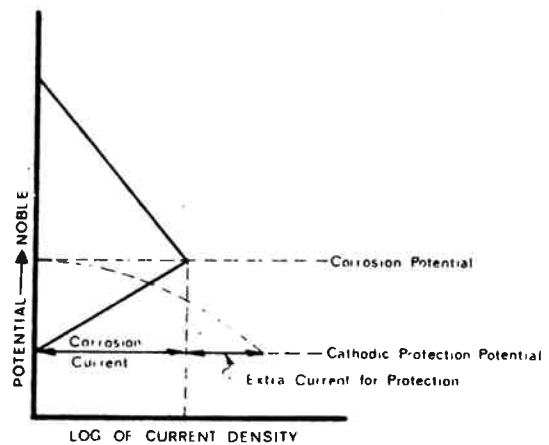
FIGURE 5 — Evans' diagram for system corroding under cathodic control.

corrosion is said to be under anodic control. In neutral solutions where the corrosion cell is often an oxygen concentration cell, the opposite situation pertains and the principal polarization occurs on the cathodes and the diagram would then have a steeply sloped cathodic polarization curve. In general, as will be shown, cathodic protection although theoretically possible, is usually uneconomical in situations where corroding systems are under anodic control. The diagrams can be used to explain this statement. If one refers to the Pourbaix diagram, it can be seen that the mixed corrosion potential of a corroding specimen will have to be moved in the cathodic direction to get it into the immunity domain. It is essential that the entire surface be rendered cathodic, and this can be achieved when the entire corroding system is made as negative as the open circuit potential of the anode. The projection of the point of intersection of the anodic and cathodic polarization curves on the abscissa represents the corrosion current, which of
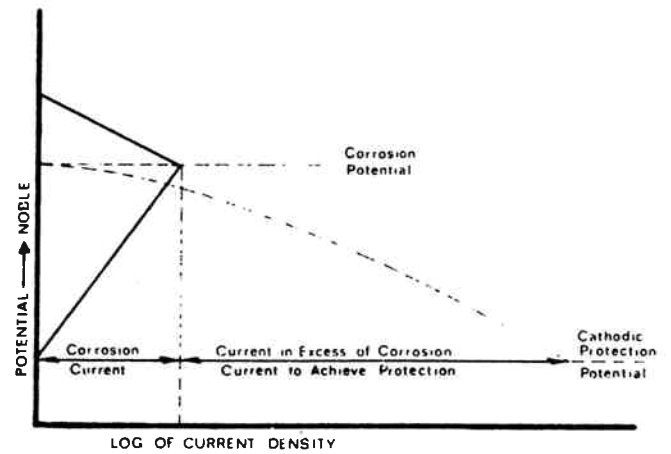
course, relates to metal loss by Faraday's equivalent, *i.e.*, the positive charge carriers in the electrolyte are metal ions. Figure 4 indicates the probable current requirements to initially achieve this situation in a system under anodic control. This current is many times greater than the original corrosion current and would no doubt result in costly electrical systems and power requirements.

If, however, the system were under cathodic control, then it can be seen in Figure 5 that very little current in excess of the corrosion current is required to shift the potential in the negative direction to achieve the open circuit potential of the anode. It is fortunate that most steel in the soil corrodes under cathodic control, and this is also typical of steel in most neutral or slightly alkaline environments.

The practical application of cathodic protection requires, in addition to a fundamental knowledge of the corrosion process, suitable design and background experience in the use of the various anode materials available, their physical arrangement and *throwing power* of different electrolytes. These problems are solved daily by electroplaters who are interested in getting current and hence metal in equal amounts on all surfaces when an object is being plated. The cathodic protection process can be thought of as a plating operation in which a monatomic layer of hydrogen is plated on the surface of the cathode.

316

The electroplater uses highly conductive solutions and relatively large current densities in his process and requires suitable anode placement to achieve good current distribution, for instance, on the interior of hollow objects. However, except for major irregularities, a highly conductive plating solution ensures a relatively uniform current distribution. In cathodic protection systems, it is rare that the conductivity of the solutions are as high as those found in plating baths, and consequently anode configuration becomes of great practical importance. It is a rule of thumb that an anode will only serve what it *sees*, but one has also to take into account the length of the current paths from the anode to various locations on the cathode and rely upon the overlapping of influenced areas on the cathode to achieve the required protective potentials. On extended cathodes such as pipelines, the resistance in the cathode may become the controlling factor in proper current distribution. It is sometimes advisable in the case of congested underground pipe runs to establish multiple negative returns in an effort to distribute protection current in shielded areas. Resistances can be inserted in these leads and adjusted to ensure equitable current distribution.

The available anode materials are varied and can be chosen to have particular advantages in a given situation, for example, graphite is available in a number of cylindrical sizes, and due to its low density loses almost 50% of its weight when immersed in water, allowing it to be suspended on its conductor. It does not, however, perform well in lower conductivity electrolytes without being installed in a special backfill material consisting of coke breeze or graphite flakes. Even when used suspended in a conductive electrolyte such as sea water, the graphite should be vacuum impregnated with linseed oil to ensure that electrochemical attack will not occur on the interior of the anode. Anodes made of 12% silicon cast iron with chromium additions are marketed as a proprietary alloy called Durco 51 and are used extensively in the ground for the protection of pipelines and in sea water for the protection of docks and jetties. Because of the high density of this material and its relative brittleness, it has to be hung on auxiliary supports and protected against impact. Lead alloyed with 3% silver is used as an anode in sea water applications where it forms a conductive surface of lead peroxide which discharges the current into the sea water preventing further anodic attack of the lead. A minimum surface current density is required to keep the lead peroxide surface intact. Titanium, niobium, and tantalum can be anodized to form highly insulating surface films and are used as electrical conductors to feed current to platinum *windows* which are plated onto the substrate. The platinum surfaces are usually a micro-inch or so thick and will discharge a predictable number of ampere hours related to the attrition of the platinum. In some cases, pure platinum can be used as an anode material, usually in the form of wire or foil, and although expensive, has a high salvage value and could be used economically in some cases for fixed periods. It is also possible to use metals, which will dissolve electrochemically, as anodes. Aluminum is popular and is consumed at the rate of approximately 10 pounds per ampere year, producing aluminum hydroxide, which although not poisonous, may be an undesirable process contaminant. The consumable anodes have an advantage in that they do not evolve oxygen at their surface, and therefore would not contribute to the total amount of dissolved oxygen in an electrolyte.

The insulation of the electrical conductors used to feed current to the anodes usually limit the use of an anode in any given environment. The substances formed at the anode due to the electrolysis of the electrolyte are usually extremely active substances, such as nascent oxygen and chlorine; in addition, the immediate environment of the anode becomes increasingly acidic. Commercial anode manufacturers use high molecular weight polyethylene, high and low density polyethylene, PVC, and fluorinated hydrocarbons as insulating materials. The chemical resistance of each of these materials must be related to the expected environment with regard to its aggressiveness and temperature. Since there is a tendency for current to discharge preferentially from the ends of the anodes, special precautions are usually taken to protect the connection end by various encapsulations. In process vessels, cathodic protection has had only limited success, mainly due to the problems in maintaining the integrity of the electrical conductors to the anodes and locating the anodes in such a way that they can properly serve the cathodic surfaces and yet not interfere with the process stream.

It can be seen from an examination of a Pourbaix diagram that the potentials required to render the surface immune from corrosion are theoretically dependent upon pH, but they are also dependent upon other factors in the environment, for example complexing agents. Unless experience has shown that the maintenance of a certain potential prevents corrosion, then each situation should be examined on its own merits and tests undertaken using a potentiostat to determine the required protective potential and at the same time the current density for its maintenance under conditions simulating the service conditions under which the cathodic protection will be applied. In industrial plants, cathodic protection can be used to protect the interior of storage vessels, heat exchanger tube sheets, underground yard piping, underground fuel storage tanks, clarifiers, settling tanks, portions of waste water disposal systems; in fact, any metal in contact with an electrolyte that is not too complicated in shape. The protective potential that must be achieved and the total current required for satisfactory operation will, of course, influence the economics of the scheme. It is often possible to use protective coatings in conjunction with cathodic protection which may produce more favorable economics. For example, a bare storage tank holding a poorly conductive neutral electrolyte, say boiler feed water, may require 30 anodes to achieve effective current distribution over the interior surface and a current density of 20 mA per sq ft of exposed cathode surface. If a suitable lining were installed in the tank, it might be possible to provide adequate supplementary cathodic protection using a single centrally placed anode and a small percentage of the original current. Of course, this would depend upon the thoroughness of the lining job. The lining would have to have good electrical insulating properties, and in addition to being able to withstand continuous immersion, must also be able to withstand the application of the cathodic protection current. The electrochemical reactions at the cathode produce a concentration of hydroxyl ions which can raise the local pH into the 11 and 12 range. If, in addition to this caustic concentration, the overpotential of hydrogen is exceeded, then hydrogen gas will actually bubble from the surface. Because of the small size of the hydrogen ion, it can easily penetrate coatings After the ions discharge and combine to form hydrogen gas, this is trapped beneath the coating. If the coating is flexible, bubbles will form which will increase in size, resulting in the separation of a great

deal of the coating from the substrate. With brittle type coatings, this does not occur since the hydrogen gas breaks through the coating without forming a bubble in the coating. If the cathodic protection system is operating at a constant current, then the degradation of the coating will result in automatic lowering of potentials such that further hydrogen is not produced. In this particular example, the anode materials would have to be chosen so that they do not contribute a detrimental corrosion by-product into the boiler feed. Oxygen is also produced on the surface of inert anodes and would be considered an undesirable boiler feedwater contaminant.

In sea water and other electrolytes containing quantities of carbonates or bicarbonates, it is possible to plate out solids on the surface of the cathode which, if allowed to remain on the surface, will in time greatly reduce current requirements. This deposit is called a calcareous deposit and is often tightly adherent and protective. If this build-up becomes too thick, it may spall off the surface and could prove a nuisance in a process stream, but of course would not be a problem when cathodic protection is applied to the external portions of buried or immersed structures.

Anodic Passivation

A number of metals exhibit what is known as active-passive transition when moved through a range of potentials while immersed in an electrolyte. The curves of current density vs potential (polarization curves) can be produced using a potentiostat and suitable recording equipment. A typical polarization curve is shown in conjunction with a Pourbaix diagram in Figure 6. It can be seen that the potential of the metal specimen was moved through a region of immunity, through a region of corrosion, and into a region of passivity. Since the polarization curve is really a plot of resistance, it is evident that a great change in resistance occurs at a potential of +100 mV as the potential of the specimen is moved into the thermodynamic region of passivity. The interpretation of this curve suggests that a change has taken place on the surface of the metal that exhibits a greatly increased resistance to current flow, and the current that continues to discharge from the specimen in the passive region keeps this passive film in repair. Stainless steels of the 300 series are self-passivating, but some of the steels in the 400 series require passivation treatment such as dipping in nitric acid to set up the oxidizing reactions that are required to form the passive film. It is possible to form this film electrically, if the metal has the required properties and the electrolyte is suitable. Mild steel, stainless steels, titanium, and many other metals in the transition group behave in this manner so anodic passivation using potentiostats constitutes another electrochemical tool for the control of corrosion. Many commercial applications have been made in sulfuric acid storage and cooling systems. This technique is also applicable in sulfate pulping digesters made of mild steel and in a number of fertilizer solutions in mild steel containers. Some of these passivating films are very durable, such as the anodized layer that can be produced on aluminum. The passive films that are formed electrochemically on mild steel in concentrated sulfuric acid will endure for a considerable period on_ the wetted surfaces of storage vessels. The films will decay with time, initially exemplifying a rapid change of potential in the active direction after the cessation of current discharge, and then a very slow potential decay until a potential is reached in the active region. This point at which the rate of potential
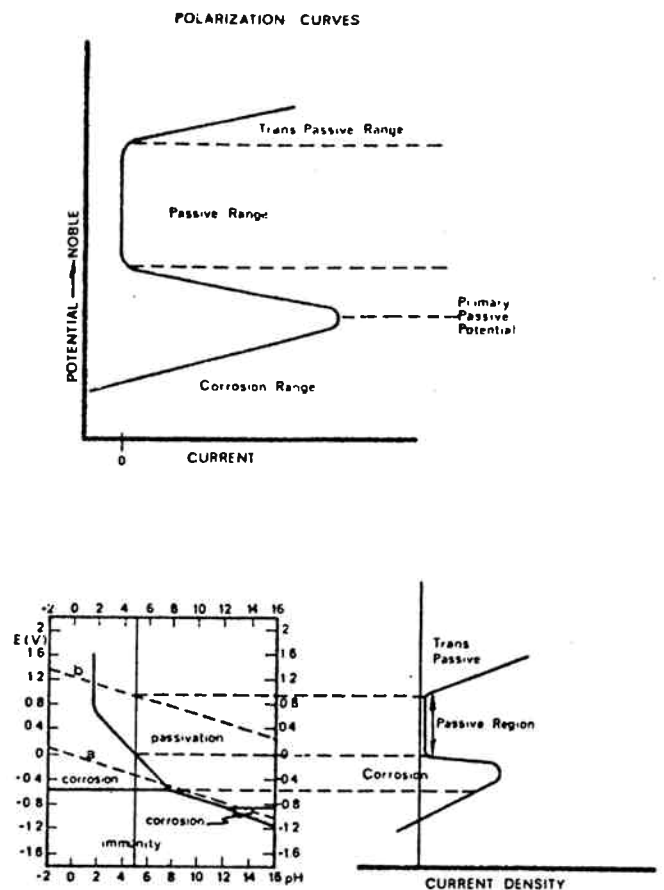

POLARIZATION CURVES

FIGURE 6 — Pourbaix diagram in conjunction with a polarization curve.

decay changes is known as Fladé arrest, a title that is sometimes given erroneously to the potential where the maximum current density is achieved in an active-passive transition. The current required to passivate the surface is usually an order of magnitude greater than the current required to maintain passivation once achieved. Since the passivation of a surface is essentially a coulomb effect, it is possible to achieve passivation with smaller applied currents over longer periods. This, of course, results in corrosion since the current discharge is taking place from the metal while it is in its active condition and relates to the rate of corrosion by Faraday's law. When a surface is passivated by the application of external current, it is important that the system be monitored to ensure that the potential remains within the passive region, since if it is made too anodic it will corrode in the transpassive region, and if it has insufficient current, it may slide into the active region, in which case it will again corrode due to the application of the holding current and in addition, suffer the self-corrosion that would be inherent in its active state. It is possible to up-grade stainless steels by means of this technique by deliberately holding their potentials in the passive range where loss of passivity would normally be achieved due to the nature of the electrolyte. In general, anodic protection techniques do not work in chloride solutions since an increase in chloride ion concentration demands a corresponding increase in maintenance currents and hence, corrosion. In fact, at sufficiently high chloride ion concentrations, the characteristic shape of the active-passive transition curve disappears entirely. A typical change in the current required to maintain passivity is shown for increases

in chloride ion concentration (Figure 7).

If anodic protection is used in vessels containing process streams, it is important to understand that the potential range of the passive region will be dependent upon various chemical factors in the process stream. If a loss of control for instance caused a sudden shift in pH, it may be possible to move into an actively corroding region without a potential change occurring. If the original conditions were then restored. the condition of the vessels walls may be such that the current available in the controlling unit may not be sufficient to repassivate the vessel. For these reasons. anodic protection must be used with caution, even by those familiar with the underlying electrochemical theory.

Corrosion Rate Determination

Electrochemical techniques can be used to give instantaneous read-outs of corrosion rates in aqueous solutions, and commercial instruments are available for this purpose. The underlying theory governing this application involves the Stern Geary equation:

$$\frac{\Delta E}{\Delta i_{App}} = \frac{\beta_a \, \beta_c}{2 \cdot 3 \, (i_{corr}) \, (\beta_a + \beta_c)}$$

It is found that for small changes of potential on a corroding specimen on either side of its natural corrosion potential (less than 10 mV). that a linear relationship exists between the potential of the specimen and the applied current. In the equation, β_a and β_c are the Tafel slopes of the anodic and cathodic reactions. where i_{corr} is the corrosion current that would flow in the system when in equilibrium with its environment and hence can be related to the corrosion rate of the system. The Tafel slopes are the slopes of linear portions of the polarization curves in which the specimen potential is plotted against the logarithm of the current density. The equation is not sensitive to the change in β values, and estimates can be made of average β values that are to be found in a great number of corroding systems.

If the $\beta_a = 0.12$ V $= \beta_c$, then the Stern Geary equation would reduce to

$$i_{corr} = \Delta i \times \frac{0.026}{\Delta E}$$

This equation is the basis of some commercially produced corrosion rate instruments that give instantaneous read-outs in aqueous systems. They are very useful for measuring very small corrosion rates or monitoring changes in aqueous process streams. Experience indicates that this technique and the instruments available can be used for reliable corrosion rate measurements.

Understanding of the thermodynamic possibilities outlined on the Pourbaix diagrams, together with a knowledge of the electrochemical basis of polarization curves will make available procedures and techniques for corrosion control.

DISCUSSION SUMMARY

H. A. Webster emphasized the problem of maintaining the electrical connection under immersion conditions in process application of anodic protection.

CURRENT DENSITY
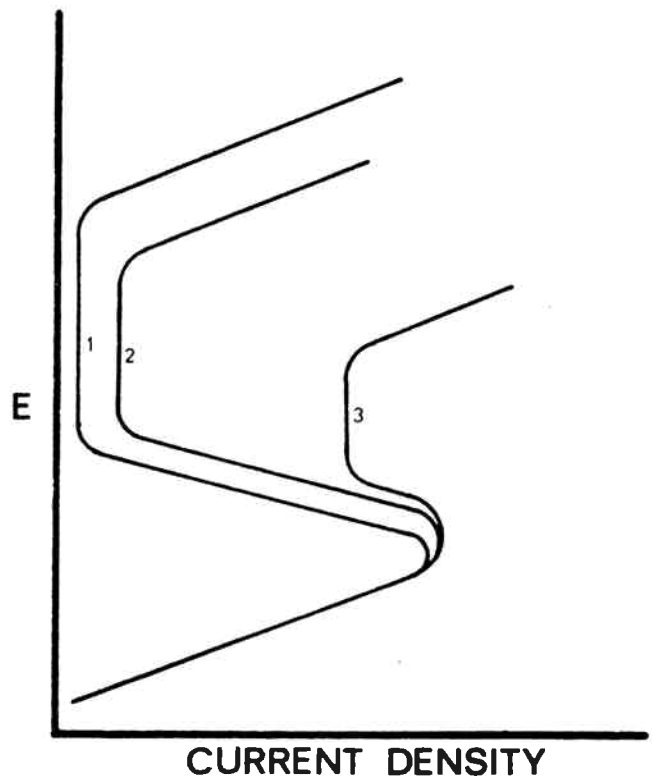
1 No chloride ions present.
2. A low concentration of chloride ions.
3 A high concentration of chloride ions

FIGURE 7 — Changes in current required to maintain passivity due to increases in chloride ion concentration.

In response to a question by A. S. Krisher, H. A. Webster discussed the successful application of anodic protection to the shell-side of a stainless steel exchanger in sulfuric acid service. However, most applications are in simpler geometry (e.g., steel tanks). Failure to maintain uniform current density and potential at all locations in a vessel can lead to catastrophic corrosion.

Cathodic protection is effective in arresting stress corrosion cracking (as opposed to hydrogen cracking) in laboratory work. Applications in complex vessels or in electrolytes of low conductivity are less reliable because of the problem of achieving uniform current density.

C. P. Dillon reported stress cracking of 18-8 tube-bundles simultaneously with galvanic corrosion of their steel shells, demonstrating the inadequate current distribution even in a conductive water. H. A. Webster emphasized that cathodic protection of water-boxes using sacrificial anodes is an established practice. However, the current will only *throw* one or two tube diameters down the tube. For the similar reasons, anodes installed in nozzles will not protect a tube-bundle.

The use of cathodic protection for rebar in concrete is currently under investigation, notably by the California Highway Dept. Duriron anodes cemented in bridge decks are utilized in a coke-filled asphalt. Current densities of fractions of a mA/sq ft are apparently effective in concrete.

C. P. Dillon emphasized that cathodic polarization is a hydrogen phenomenon. dependent upon continuous immersion. In anodic protection of steel in strong sulfuric acid, however, a semi-permanent insoluble film is produced. H. A. Webster indicated that the passive film could survive

for extended periods in the vapor phase. In lesser concentrations of acid, e.g., 60%, continuous immersion and continuous current discharge from the vessel surfaces. Liquid vapor line attack may be possible, requiring coating or lining of these areas.

Anodic protection is limited to combinations of metals and environments which have the active-passive transition characteristic.