Technical Section

Role of Polarisation Studies in Corrosion

By K. S. RAJAGOPALAN

Central Electrochemical Research Institute, Karaikudi.

POLARISATION may be defined as the change in potential of an electrode which results from current flow to or from the surface. This does not refer to changes brought about in a completely thermodynamically reversible manner in which case every infinitesimal change will be accompanied by the establishment of a state of reversible equilibrium and the potential of the electrode will obey the Nernst equation. For the Nernst equation to hold good, the process must be maintained reversible throughout its course by infinitely slow reaction and this can be applied in practice only to those cell processes which approach equilibrium at measurable rates, as, for example, the potential of a hydrogen or quinhydrone electrode. We are concerned, at present, with changes in potential taking place in processes which are far from reversible or more simply irreversible processes. In fact, nearly every electrode reaction of practical importance is irreversible to some detectable degree. The degree of irreversibility is measured by departure of the electrode potential from the reversible value under the same conditions of temperature, pressure and concentration. The principles concerned with the occurrence and magnitude of polarisation are different from the laws of reversible electrode phenomena.

The Electrochemical Theory of Corrosion

The electrochemical theory of corrosion postulates that there are two kinds of areas on a metal surface, those at which the metal goes into solution otherwise known as anodic areas and those where hydrogen discharge or oxygen absorption takes place otherwise known as cathodic areas. This assumes the existence of inhomogenity at the metal-solution interface, for otherwise no differences should exist. This inhomogenity is believed to be caused by a number of factors such as impurities in the metal, stress differences and a number of other environmental as well as metal factors including differences in crystal structure. It has been experimentally proved that these different areas have also different potentials. So, if a metal is placed in a conducting solution current will flow between the different potential areas. What are the consequences? To quote an example, let us take zinc, a metal with which we are very frequently concerned, in a slightly acidic solution which has been freed of all dissolved gases. One of the reactions which should occur is $Zn \longrightarrow Zn^{++} + 2e$, the other reaction that will take place is $2H^{+} + 2e \longrightarrow H_2$, and this reaction should, according to thermodynamics proceed till the thermodynamic potential of zinc is observed when equilibrium would be established. It is well known that despite a favourable energy relationship it does not proceed to equilibrium. In fact, the thermodynamic potentials of E Zn and EH are such that at no concentration we can imagine that they two will attain a common potential. Yet, in so far as two different potentials cannot simultaneously exist on a metal surface placed in a conducting solution, the mechanism by which the difference in potentials is eliminated has to be understood. The measured potential corresponds closely to the standard potential of zinc though zinc ion concentration in solution is far removed from that of a 1 N solution. The hydrogen reaction may then be said to be polarised. In general, when the measured potential of an electrode corresponds to the thermodynamic potential of one of the possible reactions, the other reactions are said to be polarised. When the measured potential does not correspond to the thermodynamic potential of any of the possible reactions at the electrode surface, all the reactions are said to be polarised.

The Evans Diagram

Let us now consider the polarisation behaviour of the local cells on a corroding metal surface. As mentioned earlier, current will flow between different potential areas so that the potential dif-

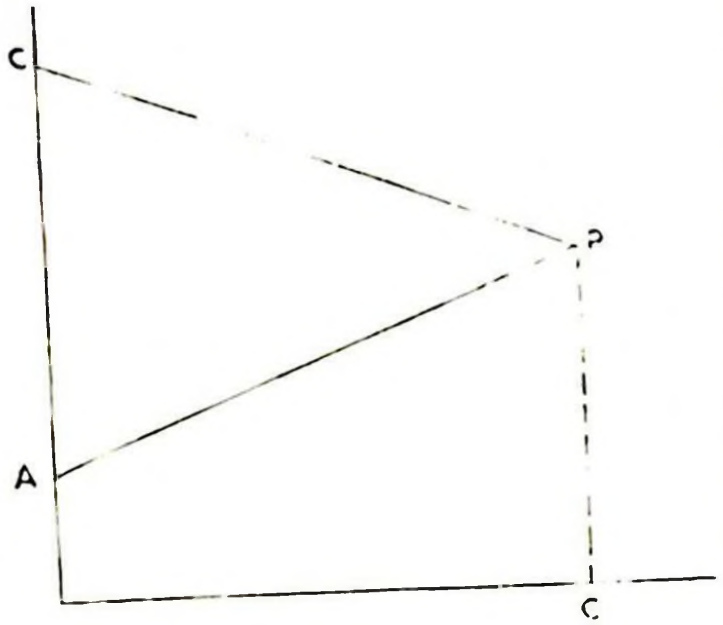


FIG. 1

ferences are annulled. As a result of this current flow the two areas will be polarised The anodic areas will become more cathodic and cathodic areas will become more anodic as shown in the diagram. (Fig. 1 . The maximum current obtainable is given by the intersection point P of the curves since this current will reduce the e.m f to O; no stronger current can flow. In the case of dilute salt solutions the current obtained may be appreciably below the maximum value given by the intersection. The current will attain such a value that the residual e m.f. between the anodic and cathodic areas exactly balances the voltage difference necessary for forcing current I through a resistance R. When R is low as in acid and highly conducting salt solutions the value will be given approximately by the intersection of the two curves. The corrosion rate is given by the current at the intersection point in Faraday gm equivalents per second. The diagram is known as the Evans diagram.

A straight line relationship between potential and current indicated by this diagram is correct only where the irreversibility of the electrode process is small. Usually, we are concerned with the electrode processes which are more irreversible and there the change in potential, or overpotential is related to the current by the equation $\eta = a + b \log i$, where a and b are constants. This is the well-known Tafel equation. Even here, when the range of current density considered is small, a more approximate equation $\eta = a^1 + b^1 i$, where a^1 and b^1 are constants dependent on the c. d. range can be used. Thus, over any small current density range overpotential is linearly related to current density. The Evans diagram has been found to be very helpful in the understanding of corrosion processes. Firstly, the Evans diagram tells us that the potential of a corroding metal lies somewhere between the equilibrium values of the oxidation-reduction systems which are operative. This potential is known as compromise potential or corrosion potential. Secondly, its value is dependent on the shape of the anodic and cathodic polarisation diagram. Thirdly, at this potential the rates of the anodic and cathodic reactions are equal. Fourthly, the steady corrosion rate of a metal is equivalent to the current corresponding to this potential. Further, if the polarisation effects at the cathodic areas influence the corrosion velocity while those at the anodic areas do not, then according to Evans the system is under cathodic control. Conversely, if the irreversible effects of the anodic areas influence the corrosion velocity while those at the cathodic areas do not, the system is under anodic control. In actual measurements, voltage effects caused by ohmic drops have also to be included. If anodic and cathodic polarisation are negligible as compared to ohmic drop the system will be under resistance control. The advantages of knowing the Evans diagram of a metal in any environment is thus apparent. Unfortunately, all methods of obtaining the information necessary for the construction of this important diagram have been limited to cases where the local anodic and cathodic elements could somehow be isolated. But then, in most practical systems it is physically impossible to isolate the local elements without causing profound alteration in the behaviour of the system.

Polarization Studies

One of the methods that have been employed where it has not been possible to isolate the local anodic and cathodic elements is known as the potiential-break method. In this method it is assumed that a sharp change in the slopes of the polarisation curves takes place as potential differences on the metal surface are made to disappear as a result of polarisation of the metal surface either anodically or cathodically. If these were so it should be possible to get by the potential-break method, the open circuit potentials of the anodic and cathodic areas which together with the corrosion potential can give some idea of the slopes of the polarization curves. But it was observed by Logan[1], when he examined various methods of plotting cathodic polarisation measurements, that the potential-break method indicated a different current requirement for complete cathodic protection than that required in

practice. Further, breaks could be obtained regardless of whether the potential was plotted as a linear or logarithmic function of applied current. In a number of systems it was also observed that smooth curves rather than a series of straightlines are obtained. Stern[2] has analysed the shapes of polarization curves obtained by external application in terms of modern concepts of electrochemistry. The analysis and the equations drawn by him are as follows: when a non-corroding metal at equilibrium potential is polarised by application of external cathodic current and the change in voltage is plotted against applied cathodic current on log scale, deviation from Tafel slope exists as long as the reverse (oxidation) current of the reaction $Z^+ + e \rightleftarrows Z$ is significant in comparison to the forward or reduction current at magnitudes of exchange current and other voltage commonly found. Reliable estimates of the Tafel constants require measurements in the region of 1000 times the exchange current. In this region the situation may become complicated by two interfering phenomena, concentration polarisation and resistance drop effects. If the reduction current is 1/10th the limiting diffusion current or more, concentration polarisation starts to become significant experimentally. Under these conditions, a practically smooth curve which can be easily divided into three distinct straightline regions and in which considerable latitude can be exercised in the choice of the break positions is obtained. The position becomes more confused when a corroding electrode is taken for consideration. Two co-existing electrochemical reactions now appear: $Z^+ + e \rightleftarrows Z$, and $M^+ + e \rightleftarrows M$, each of which has its own exchange current and Tafel slope. The steady state potential of the corroding metal occurs when the total rate of oxidation equals the total rate of reduction. The externally applied cathodic current is equal to the difference between the sum of the rates of all the reduction reactions and sum of the rates of all oxidation reactions. True Tafel behaviour is not evident until polarisation currents of the order of several times the corrosion current are applied, and if concentration polarisation and resistance drop effects are also considered, any observable Tafel behaviour may also be completely eliminated. From these analyses, he concluded that an approach to polarisation data in terms of breaks or of Tafel relationship is not likely to be fruitful for most corrosion studies.

Another method that has been suggested in order to find out the open circuit potentials of anodic and cathodic areas is described by May and LaQue[4]. In this method, the rate of corrosion of metal is found by weight loss experiments at various values of applied current when the metal is cathode. Then the change in potential at different values of applied current as well as the corrosion rates are plotted as shown in Fig. 2. The corrosion rate vs applied current curve is extrapolated to that value of current at which the corrosion rate is zero, and the potential corresponding to that applied current is taken as the potential at which all the cathodes disappear from the surface and the metal has become completely anodic. This is expected to give the open circuit potentials of the local anodes. To obtain the open circuit potential of the local cathodes, the corrosion rate calculated from weight loss measurements when the metal is polarised anodically at different values of applied current is plotted against applied current and in the same figure the corrosion rate calculated from applied current value is also plotted. The two curves thus obtained may be extrapolated to the point at which they both meet; at this point local action may be considered to be due to the applied current. From this, it is concluded that this point represents the state wherein local action has disappeared as a result of the metal becoming cathode. The potential at which this point is obtained can, therefore be looked upon as the open circuit potential of the cathodes. While this method appears to be a promising approach to the elucidation of Evans diagram, it has apparently not found any favour with those working on the polarization behaviour of corrod-

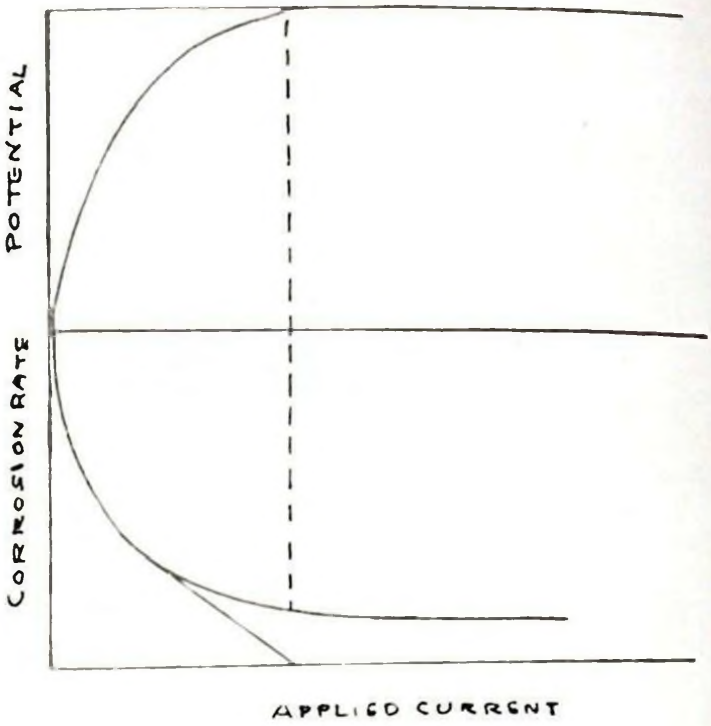


FIG. 2

of aluminium by various pretreatment processes, chromate treatment of zinc, and phosphate and wash primer treatments for steel. Both the potential and polarisation data have been satisfactorily explained making use of this interpretation. It has been shown that the greater steepness of the anodic and cathodic polarisation curves of zinc after chromate treatment arises from the decrease in the anodic and cathodic areas. Usually, when the surface is subjected to some kind of chemical treatment it is expected that the total area of metal surface will be increased and consequendy the current density will fall as a result of which the polarisation will decrease On the other hand, when the metal surface is passivated the available area for carrying out the polarisation gets diminished and the polarisation is rendered steeper. The mecha nism of inhibition by chromate inhibitor has also been explained in this way. However, so far it has only been possible to give a more or less qualitative interpretation of the observed phenomenon relating to various pretreatment processes. It is necessary to obtain quantitative experimental verification of the validity of the equation obtained from the application of the rate theory with respect to a number of practical systems. Work in this direction is in progress.

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