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### How Instant is Instant?

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#### Abstract

The instant off technique for the determination of the value of the potential to which a metal has been polarised by the action of a cathodic protection current implicitly relies on the time scales of the various polarisation decay processes being very different. Normally measurements are taken between 0.1 and 1 second after the interruption of the current and the assumption is made that in this time the activation and diffusion polarisations have not decayed by a significant amount. This paper attempts to calculate the time constants for the decay associated with the ohmic, activation, and diffusion components of the polarisation. It suggests that there may be such an overlap between the different decay processes that differentiation between them is not possible. The calculations when applied to steel in sea-water and reinforcing bars in concrete suggest that such is the difference between these typical systems that generalised criteria are not possible.

**Keywords:** cathodic protection, potential, criteria, instant off, overpotential, activation polarisation, diffusion polarisation, ohmic polarisation.

## Introduction

The "instantaneous off" technique for the determination of the potential to which a cathodically protected structure has been polarised has been used for at least fifty years and is the basis for national standards in a number of countries. Typically, Australian Standard AS 2832.5 records that protection is obtained on the Absolute Potential Criterion when, "An instant off potential (measured between 0.1 s and 1 s after switching the d.c. circuit open) more negative than  $-720$  mV with respect to Ag/AgCl/0.5M KCl." is obtained. It seems to be generally assumed that the ohmic component of the polarisation dissipates in times that are very much shorter than the activation and diffusion components of the polarisation, and although it is the combination of the activation and diffusion components of the overpotential that moves the potential of the metal being protected to a value corresponding to a lower corrosion activity, the relative magnitudes of these components and therefore the means to modify them remains unclear.

Neglecting any uncertainties in the ability of the switching system to provide a step discontinuity in the current there are in general four separate decay processes in the polarisation decay process. These are, the activation, concentration and resistance polarisations and the capacitive effects of the electrolyte in which the system is immersed. It has sometimes been assumed that the decay constants for these are well separated in magnitude. Polak [1] suggested that the ohmic component of the polarisation potential disappears in picosec whereas the electrochemical component (activation and concentration overpotential) disappears in the interval from 10 millisec up to several seconds. Schwenk [2] calculated that the time constant for the activation component of the polarisation was between  $10^{-5}$  and  $10^{-1}$  sec. but did not attempt the calculation of the time constant for the concentration polarisation. Wallen and Linder [3] suggested that because the time constant for the decay of the ohmic component of the polarisation overpotential could be of the order of milliseconds then it was not possible with the instrumentation that they had

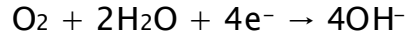
available to them at that time to separate the IR drop from from the other kinds of polarisation. Cherry [4] suggested that the capacitive effects of the soil around a buried pipeline could be of the order of seconds. The object of this paper is therefore to examine the possible time constants for the decay of activation and concentration polarisation and to suggest that the sharp differentiation between the time constants for the various potential decay processes that is assumed by a number of monitoring standards may not always obtain in practice. In particular it is concerned with the extent to which activation and diffusion polarisation play their different roles in determining the so-called absolute potential measured using instant off techniques.

In order to illustrate the relative roles played by the different components of the total polarisation two situations will be considered; bare steel in sea water and reinforcing bars in concrete.

### **Bare steel in Sea-water**

The calculations to determine the relative magnitudes of the components of the total polarisation for bare steel in sea-water will be based upon the assumption that a cathodic current of  $100 \text{ mA m}^{-2}$  results in a diffusion overpotential of 10 mV and an activation overpotential of 100 mV. Although it is a very greatly simplifying assumption, the time constant for the activation polarisation of a bare electrode in a conductive electrolyte solution can be calculated by assuming a simple Randles circuit that incorporates the polarisation resistance of the solid/electrolyte interface and the double layer capacity. Putting the polarisation resistance as  $5 \times 10^{-2} \text{ ohm m}^{-2}$  and the double layer capacity as  $1 \text{ F m}^{-2}$  [5] yields a time constant of about  $5 \times 10^{-2} \text{ sec}$ . The activation overpotential component of the polarisation falls to about 1% of its original value in about 0.13 sec and consequently is not captured by an instantaneous off potential measurement one second or even 0.1 second after the current supply to a bare metal surface in a conductive electrolyte is switched off.

The time constant for the concentration polarisation that may obtain for a similar system may also be calculated if it is assumed that the cathodic process is



and the rate determining step in this process is the transport of oxygen to the rebar surface. The diffusion overpotential is given by

$$\eta_D^c = \frac{RT}{zF} \ln \left( \frac{c_s}{c_o} \right)$$

where  $c_s$  is the concentration of oxygen at the surface of the metal and  $c_o$  is the concentration of oxygen in the external solution.  $c_s$  is determined by the balance between the rate at which oxygen is consumed at the cathode and the rate at which it can diffuse to the cathode through the solution. Hence in order to carry out the calculation for a diffusion overpotential component of the total polarisation of 10 mV, it will be assumed that the bulk solution is in equilibrium with the atmosphere and has an oxygen content of 10 mg/l. The concentration of oxygen at the surface of the metal can then be calculated to be 0.020 mg/l or 0.6 mole.m<sup>-3</sup>.

The rate of diffusion of oxygen to the cathodic surface may be assumed to follow Ficks second law of diffusion. If it is assumed that in a steady state, the rate at which oxygen is consumed at the surface corresponds to the protection current that is being applied then there will be a concentration profile in the solution. The form of this concentration has been calculated by Sands [6] and is reported as

$$c_x = c_0 - \frac{iz}{nF\sqrt{\pi D}} \int_0^t \frac{1}{\sqrt{t}} \cdot \exp\left(-\frac{x^2}{4Dt}\right) \cdot dt \quad (1)$$

where  $x$  is the distance from the electrode,  $t$  the time for which the current has been flowing,  $i$  is the current density flowing on to the surface,  $z$  is the number of the reactive molecules taking part in the reaction,  $n$  is the number of electrons involved in the reaction,  $F$  the Faraday and  $D$  the diffusion coefficient of the reactant in the solution.

Equation (1) can be integrated for increasing values of time to examine the development of the concentration profile. However for an "instant off" potential measurement the impressed current is reduced to zero, theoretically instantaneously, but in practice over a period that is determined by the efficiency of the switching gear. It will be assumed that at the moment that the current falls to zero then for a short period at least the concentration gradient of the reactants in the solution will remain and that these will cause a flow of the reactants to the metal surface with a consequent reduction in the diffusion overpotential. These concentration gradients supported the flow of reactants to the surface at a rate that corresponded to the impressed current. Hence it is suggested that initially the flow of reactant to the surface will continue at the same rate as before the current interruption but that since the reactants are no longer being consumed by the electrode reaction they will be increasing the concentration at the interface and decreasing the diffusion overpotential. The variation of the concentration at the surface of the reactant with time can therefore be calculated following Vetter [7] by putting  $x = 0$  in equation (1) and integrating to yield

$$c_s = c_o - \frac{2}{\sqrt{\pi}} \cdot \frac{iz}{nF\sqrt{D}} \cdot \sqrt{t}$$

The initial rate of change of the diffusion potential will then be given by

$$\begin{aligned} \frac{d\eta}{dt} &= \frac{RT}{nF} \cdot \frac{iz}{c_s} \cdot \frac{dc_s}{dt} \\ &= \frac{RT}{nF} \cdot \frac{1}{c_s} \cdot \frac{iz}{nF(\pi D)^{1/2}} \cdot t^{-1/2} \end{aligned} \quad (2)$$

Putting  $c_s = 0.6 \text{ mole m}^{-3}$  as derived previously, assuming that the polarising current was  $10^{-1} \text{ Am}^{-2}$  and  $D = 1.54 \times 10^{-1} \text{ m}^2\text{sec}$ . [8]. yields an initial value for  $\frac{d\eta}{dt}$  of  $9 \times 10^{-5} \text{ t}^{-1/2} \text{ V/sec}$ . Equation (2) is

only valid for the instantaneous decay rate of the diffusion overpotential component of the polarisation, but the time taken for this component to fall by 1% of its original value may be approximated by the integration of equation (2) to suggest that this may take some

25 sec. It seems therefore that an instantaneous off potential measurement carried out at between 0.1 and 1 sec is likely to capture most of the diffusion overpotential component of the total polarisation. However since the time constant for the decay of the activation polarisation has been calculated as of the order of 50msec, the magnitude of the activation overpotential component of the polarisation at one second or even 0.1 seconds after switching off the current is vanishingly small and will not be captured by an instant off potential measurement.

It may therefore be suggested that the polarisation that may be determined by an instantaneous off measurement for an electrode that is being cathodically protected in (say) sea-water is effectively entirely determined by the concentration overpotential and not at all by the activation polarisation.

## **Reinforcing bars in Concrete**

For reinforcing bars in concrete the relative magnitudes of the components of the total polarisation will be based upon the assumption that a cathodic current of  $5 \text{ mA m}^{-2}$  yields a diffusion overpotential of 100 mV and an activation overpotential of 50 mV. The approximate time constant for the decay of the activation polarisation of a reinforcing bar electrode in a concrete can be calculated as was done previously by assuming a simple Randles circuit. For a reinforcing bar in the passive state, putting the polarisation resistance as  $210 \text{ ohm m}^2$  [9] and the double layer capacity as  $31 \times 10^{-2} \text{ F m}^{-2}$  yields a time constant of 65 sec. If the activation overpotential component of the polarisation under cathodic protection had been 50 mV then this time constant corresponds to a retention of 98% of the activation polarisation and a depolarisation rate of 0.7 mV/sec at 1 second after the current has been switched off. An instantaneous off potential measurement carried out between 0.1 and 1 sec is therefore likely to capture most of the activation overpotential component of the total polarisation.

In a similar fashion, the rate of depolarisation of the diffusion overpotential for a reinforcing bar in concrete may be calculated. If it

is assumed that the original diffusion overpotential is 100 mV then by the same method as was used previously it is assumed that the concentration of the oxygen in the pore water adjacent to the electrode surface is  $0.3 \text{ mole m}^{-3}$ . Then if the diffusion coefficient for oxygen in concrete is put as  $2 \times 10^{-8} \text{ m}^2\text{sec}$  [9] and assuming that a protection current of  $5 \times 10^{-3} \text{ Am}^{-2}$  is being applied, then equation [2] yields a value for  $\frac{d\eta}{dt}$  of  $2.5 \times 10^{-6} \text{ t}^{-1/2} \text{ V/sec}$ . Hence calculating as before the time taken for this component to fall by 1% of its original value, this may be approximated as 200 sec.. It seems therefore that an instantaneous off potential measurement carried out at between 0.1 and 1 sec is likely to capture most of the diffusion overpotential component of the total polarisation.

It is therefore suggested that in contrast to the depolarisation of an unprotected electrode in solution, the polarisation that is measured one second after the interruption of a cathodic protection current contains both the activation and diffusion overpotential components. The depolarisation that may be measured in the following four hours may contain all the activation polarisation but only a fraction of the diffusion overpotential component.

## Conclusions

The "instantaneous" shift in potential that occurs when a cathodic protection current is interrupted is very rarely solely the  $iR$  drop that results from the passage of the current from the anode through the surrounding electrolyte. It will normally also contain one or more of the other components of the polarisation that is being applied to the electrode. This means that the potential that is reported as the result of such a measurement is rarely the actual polarised potential, but a potential that includes unknown portions of the activation and diffusion overpotentials.

The extent to which the subsequent drift of the potential to more positive values may be the result of the decay of activation or diffusion overpotential components of the total polarisation will depend upon the system which is being protected and it would not be wise to

assume, as has sometimes been the case in the past, that diffusion effects control this phase of the depolarisation process.

It therefore seems that the cathodic protection criteria that have been adopted, the absolute potential, the depolarisation criterion, the absolute potential after depolarisation, should all be regarded as purely empirically based and may be very dependent upon the nature of the system that is being protected.

## References

1. Polak, J. "Conference on the internal and external protection of pipes", Brit. Hydr. Res. Assn., Durham, 1975 Paper F4
2. Schwenk, W. "Determination of the potential of current-carrying electrodes with special reference to their application in cathodic corrosion protection". *Werkstoffe und Korrosion* (1962), 13 212–18.
3. Wallen, B. and Linder, B. "Ohmic Potential Drop in Cathodic Protection of Buried Structures: Evaluation of some Measuring Methods", *British Corrosion Journal*, 8, (1973), 7 – 14
4. Cherry, B.W. "An analysis of the Potential Decay when Cathodic Protection is Interrupted", 4th Asian–Pacific Corrosion Control Conference, Tokyo, 1985, 1243
5. von Baeckmann, W., Schwenk, W. and Prinz, W. "Cathodic Corrosion Protection", Gulf Publishing, 1989, 44
6. Sand, H. J. S. "On the Concentration at the Electrodes in a Solution", *Philosophical Magazine* 1, (1900), 45 – 79
7. Vetter, K.J. "Electrochemical Kinetics" trans Scripta Technica Inc. Academic Press, New York (1967), 207
8. Ferrell, R.T. and Himmelblau, D.M. "Diffusion Coefficients of Nitrogen and Oxygen in Water" *J of Chem. and Eng. Data*, 12, (1967), 111 – 115



9. Birbilis, N., Nairn, K.M. and Forsyth, M., "Transient Response Analysis of Steel in Concrete" *Corrosion Science*, **45**, (2003), 1895
10. Bertolini L., Elsener, B , Pedefferri, P. and Polder, R. "Corrosion of Steel in Concrete", Wiley VCH, KGaA, Weinheim, 2004, 42