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Potential Transmission and Transients During Corrosion:

Applications to Corrosion Monitoring

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Hugh S. Isaacs and Jeong-Hwan Cho

Brookhaven National Laboratory, Upton, NY 11973

ABSTRACT

The transmission of potential along a passive metal/electrolyte interface, which is important in corrosion monitoring, has been considered for transitory and sustained corrosion processes. The observed signals are modified and delayed by the passive surface. Using a transmission line as the equivalent circuit of a pipe and incorporating the impedance characteristics of the passive-metal/solution interface, enabled an analysis of the effectiveness of corrosion monitoring methods to be carried out.

INTRODUCTION

Corrosion monitoring techniques may be categorized as active or passive. Open circuit potential and noise monitoring products fall into the passive category. Active methods involve small perturbations, as with polarization resistance or ac impedance, that do not alter the processes taking place. Whether active or passive, the methods must emphasize local

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conditions. Although monitoring for corrosion of a real container or pipe is required, in many cases an immersed sample is used and only reflects changes in the corrosivity of the environment. Consequently it is necessary to consider what changes would result if the entire pipe or container is monitored. For example, how far does an applied ac current flow if a measurement is made of the impedance in a pipe? Alternatively, if corrosion developed within a pipe, at what distance would a reference electrode be able to detect any potential changes? This paper attempts to address some of these issues and for simplicity, considers a pipe represented by a one-dimensional equivalent circuit, analogous to a transmission line. Rebars in concrete (1), pores in electrodes (2), and wires in solution (3) are also examples with analogous circuit diagrams to that shown in Fig 1.

OPEN CIRCUIT POTENTIAL MONITORING OF SAMPLES

The open circuit potential has long been used to monitor corrosion. The influence of changes in steady-state polarization have been clearly elucidated (4,5). However, complications arise because of the important role played by the capacitance of the passive surface in non-steady-state measurements, when the potential changes. For example, following pit initiation at open circuit, the potential decreases rapidly as the pit grows. The current from the pit flows to the passive surface which supplies the necessary cathodic current. However, this cathodic current is generally too large to be accounted for by the faradaic, oxygen reduction process. It arises from the discharge of the capacitance of the passive surface/solution interface (6,7). Following pit repassivation, the capacitance is recharged as the potential increases. The recharging of the capacitance requires a

compensating cathodic current. This cathodic current is from the slow electrochemical reduction of oxygen on the passive surface which only now becomes the significant cathodic process. The rate of this slow reaction dominates the recharging of the capacitance and thus the slow rate at which the open circuit potential increases. Based on these processes, a quantification of the characteristic pitting transients with its rapid potential drop and slow potential increase can be made. It has also been shown that more complex transients can be quantitatively predicted based on the impedance of the passive surface (6).

When pits do not repassivate, the rate at which the potential drops, decreases and eventually the potential becomes steady. As the rate decreases, the capacitive current contributes less and less to the required cathodic current. Here, too, the slow oxygen reduction process supplies an increasing fraction of the required cathodic current and eventually supplies all the cathodic current when the steady potential is reached.

OPEN CIRCUIT POTENTIAL MONITORING IN A PIPELINE

The transmission line circuit shown in Fig. 1 is an electrical analogue of an internal pipe carrying water. Two points in this semi-infinite line are important: the point where corrosion takes place and the point where the potential is monitored. The potentials and currents are symmetrical about the point of corrosion and a transmission line terminating at this point can be used with appropriately halved currents flowing from the corrosion site. The simulated electrical components are calculated per unit length of the pipeline. The values of the impedance of the passive surface per unit length of pipe, Z ,

varies with frequency, and R is the resistance of the solution per unit length (ohm/cm) along the axis of the pipe.

The following discussion introduces two oversimplified potential responses, a simple potential step due to the start of sustained corrosion and, a single rectangular corrosion transient pulse, caused by a pitting-repassivation event.

Sustained corrosion

If sustained corrosion initiates at time $t=0$ (seconds) and the impedance of the interface can be considered to be a purely capacitive with a value C in units of F/cm, then a step change in potential from V_o to V_f (volts) produces a potential change along the pipe at a distance x cm from the corrosion site given by (7,8)

$$V = V_o + (V_f - V_o) \operatorname{erfc} \left\{ \frac{x}{2} \sqrt{\frac{RC}{t}} \right\} \quad (1)$$

This is similar to a diffusion equation with a diffusion coefficient of $1/RC$. In this case the potential of the entire pipe would eventually change from V_o to V_f . The rate of potential change depends on the interfacial capacity, c (F/cm²), water resistivity, ρ (ohm-cm), radius of the pipe r (cm) and the distance from the site of corrosion. Then

$$RC = \frac{\rho}{\pi r^2} 2\pi r c = 2 \frac{\rho c}{r} \quad (2)$$

Taking a solution resistivity of 10000 ohm-cm, a 50 μ F/cm² interfacial capacitance and a radius of 5 cm for the pipe, then the potential would reach a value midway between V_o and

V_f within a minute at a distance of 5 cm and at 1000 cm in 2 days.

For a purely resistive interface the potential changes are immediately transmitted along the pipe. However, the distance over which a significant potential change is seen is limited. Taking the interfacial resistance as R_i ohm/cm in series with an emf equal to the prior open circuit value V_o , and a potential of the corrosion site V_f , then the potential at a distance x from the corrosion site is given by (9)

$$V = V_o - (V_o - V_f) \exp \left(-x \sqrt{\frac{R}{R_i}} \right) \quad (3)$$

If the interfacial resistivity is given by Ω , then

$$\frac{R}{R_i} = \frac{2 \rho}{r \Omega} \quad (4)$$

Hence, from Eq. 3 the potential change at a particular distance x , increases with decreasing solution resistance, decreasing pipe diameter and increasing interfacial resistivity. Taking the interfacial resistivity of the passive surface as 10^7 ohm-cm² and the same solution resistivity and pipe diameter as above, a significant potential change of >10% due to the corrosion will be observed up to about 120 cm.

Transitory Corrosion

Potential transients, associated with the onset and repassivation of localized corrosion, have been considered as noise (10,11) and their frequency spectrum, a method of corrosion monitoring. In a pipe a representative transient would not be observed, as its

shape has a strong dependence on the distance of the reference electrode from the site of corrosion.

Eq.1 can be expanded to analyze the changes in response of a rectangular corrosion transient (3,8) in a pipe with capacitive passive interface. In Fig. 2 a series of responses at increasing distances from the source are shown. The magnitudes of the potentials and the sharpness of the response decrease rapidly with distance. The transmission line acts as a filter, removing the high frequency components of the originating transient, and the amplitude of all the lower frequency components decrease exponentially with distance from the source (12-14). If such breakdown sites take place along a pipe any noise analysis will be a conglomerate of the component frequencies of these curves and the low frequency components are most important.

In the case of a purely resistive interface the magnitude of the potential change again varies with distance from the corrosion site according to Eq. 2. The shape of the signal would, however, remain the same as that at the corrosion site. This assumption will generally be a poor approximation because short times are involved, and the capacitive components of the interface would then dominate the impedance.

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DISCUSSION

The analysis shows that the potentials measured at a distance from the site of corrosion are markedly changed down a pipe. A means for calculating these effects is also given. In the examples provided, only purely resistive or capacitative interfaces were considered. With true surfaces, the impedance is a complex function of the frequency and more accurately predicted responses require Fourier analysis of the potential at the corrosion site and the summation of the modulated components for each frequency at the required distance from the source. This has been done for a passive steel surface which has a constant phase angle impedance character over a wide range of frequency (14).

The examples given do indicate that under certain circumstances, where the interface shows a high impedance, open circuit potential measurements may monitor over relatively long distances. Impedance measurement can be used to detect the location of a corrosion site (1). However, where the impedances are low and not capacitative, the range of influence of a corrosion site is restricted. The low surface impedance may arise because of rapid electrochemical reactions. These may involve general corrosion or a reversible redox reaction. In high temperature water above 200°C, stainless steel surfaces show low resistivities and high resistivities at lower temperature. No electrochemical detection of stress corrosion cracking is made at and above 200°C but transients at low temperatures due to cracking are clearly observed (15). This example demonstrates that an understanding of the electrochemistry of a system is required both because of its effects on determining the

impedance characteristics of the metal interface and the choice of corrosion monitors as well as on the possible modes and causes of corrosion.

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REFERENCES

- 1) D. D. Macdonald, M. C. McKubre and M. Urquidi-Macdonald, *Corrosion*, **44**, 2 (1988).
- 2) R. deLevie, in *Advances in electrochemistry and Electrochemical Engineering*, Edt P. Delahay, Vol. 6, Interscience Publishers, 1967, p 329.
- 3) H. S. Isaacs and A. J. Davenport, *J. Electrochem Soc.* **137**, 2196 (1990).
- 4) U. R. Evans, *The Corrosion and Oxidation of Metals*, Edward Arnold (Publishers) Ltd., 1960, p 874.
- 5) O. Gatty and E. C. R. Spooner, *The Electrode Potential Behavior of Corroding Metals in Aqueous Solutions*, Oxford University Press, 1938.
- 6) H. S. Isaacs and Y. Ishikawa *J. Electrochem Soc.* **132**, 1288 (1985).
- 7) H. S. Isaacs, *Corrosion Sci.*, **29**, 313 (1989).
- 8) H. S. Carslaw and J. C. Jaeger, *Conduction of Heat in Solids*, Oxford University Press 1959, p 69.
- 10) U. Bertocci and J. Kruger, *Surf.Sci*, **101**, 608 (1980).

- 11) C. Gabrielli, M. Keddam, M. Krarti, C. Pallotta, *Computer Acquisition and Analysis of Corrosion Data*, Proceedings Vol. 85-3, M. W. Kendig, U. Bertocci and J. E. Strutts, Eds. The Electrochemical Society Inc., Pennington, NJ, 1985, p 210.
- 12) C. Fiaud, M. Keddam, A. Kadri and H. Takenouti, *Electrochimica Acta*, **32**, 445 (1987).
- 13) J. H. Cho, H. S. Isaacs and A. J. Davenport, The Electrochemical Soc. Meeting Vol 89-2, Hollywood, Florida, Oct., 1989, Extended Abstract 147.
- 14) J. H. Cho and H. S. Isaacs, to be published.
- 15) H. S. Isaacs, *Surfaces, Inhibition, and Passivation*, Proceedings Vol. 86-7, E. McCafferty and R. J. Brodd, Eds. The Electrochemical Society Inc., Pennington, NJ, 1986, p 440.

Figure 1. Transmission line equivalent circuit of a site of corrosion in a pipe.

Z is the impedance of the passive surface per unit length of pipe and R is the resistance of the solution per unit length of pipe.

Figure 2. Simulated potential transients at distances of 1 to 5 in units of magnitude $2\sqrt{1/RC}$. The initiating transient was a negative rectangular potential pulse of unit magnitude lasting for 0.7 time units.

Fig. 1

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FIGURE
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