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An Electrochemical Method for Measuring Localized Corrosion under Cathodic Protection

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A new method has been developed to measure metal corrosion rates and their distribution under cathodic protection (CP). This method uses an electrochemically integrated multi-electrode array to take local measurements of cathodic current density while simulating a continuous metallic surface. The distribution of cathodic current densities obtained under CP was analyzed to estimate the anodic current component at each electrode of the array. Corrosion patterns determined by this new method have shown good correlation with visual inspection and surface profilometry of the multi-electrode array surface.

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Although cathodic protection (CP) is widely used in corrosion prevention, conditions that are often encountered in practice such as stray currents¹ or CP currents shielding^{2,3} could significantly affect its effectiveness. Unfortunately, methods to evaluate corrosion rates under CP are uncommon and seriously limited. Conventional metal loss measurements can only provide time averaged corrosion information while electrical resistance probes are generally not appropriate for localized corrosion evaluation. Traditional electrochemical methods for measuring corrosion rates such as linear polarization resistance are not directly applicable to perform measurements under CP because their fundamental relationship, i.e. the Stern - Geary equation,⁴ is only valid near the Open Circuit Potential (OCP).

One of the first attempts to overcome this limitation was made by Stern and Geary,⁴ who described a method for estimating corrosion rates under cathodic polarization conditions. This method involves the indirect determination of the anodic Tafel coefficient based on the system's cathodic polarization curve, and the use of this coefficient to extrapolate the anodic Tafel behavior. Stern and Roth⁵ experimentally confirmed this method by measuring corrosion rates of steel in acidic environments under CP with reasonable success. Many variants of this method have been subsequently proposed; however these methods were shown to be very sensitive to noise and potential drops.^{6,7} An important limitation that these methods share in common is that they are limited to systems where the cathodic reaction is strictly charge transfer controlled.⁸ Since in many practical applications the cathodic reaction kinetics are controlled by the diffusion of reactants, Barbalat et al.⁹ have recently attempt to expand the applicability of the method proposed by Stern and Geary⁴ to aerated soil by modifying the model used to describe the cathodic reaction. Another limitation of these methods is that they are based on ideally homogenous electrodes and could only provide spatially averaged corrosion information. In an attempt to evaluate the maximum local corrosion rate produced under CP, Sun^{10,11} used the method developed by Yang et al.¹² based on a coupled multi-electrode array to estimate the largest anodic current density based on statistical parameters by assuming that the local current densities measured at each electrode follow a normal distribution. Unfortunately they did not correlate individual local current density values with visual observation of localized corrosion damage on the array.

Theoretical Basis of a New Data Analysis Method

Here we present a new method for analyzing data obtained from an electrochemically coupled multi-electrode array in order to determine local corrosion rates and their distribution under CP. The electrode array simulates a continuous metallic surface and allows the measurement of the CP current supplied to each individual electrode. Figure 1a shows a schematic Evans diagram for a single carbon

steel electrode from such electrode array. As indicated in the figure, I_A is the cathodic current density required to polarize the electrode from its corrosion potential (E_{corr}) to a desired CP potential (E_{CP}), and this is equal to the difference between the anodic ($I_{a,\text{CP}}$) and the cathodic ($I_{c,\text{Lim}}$) current densities at E_{CP} . When a multi-electrode array is used (Fig. 1b), slight metallurgical or electrochemical heterogeneities throughout its surface would produce differences in the anodic behavior of each electrode and consequently, different anodic current density values ($I_{a,\text{CP-A}}$, $I_{a,\text{CP-B}}$ and $I_{a,\text{CP-C}}$) at E_{CP} . Under oxygen diffusion controlled conditions, the cathodic reaction kinetics are determined by the oxygen flux, and therefore the same cathodic current density ($I_{c,\text{Lim}}$) should result on all electrodes (i.e. the same 'baseline' value), provided they have the same access to oxygen. Under these conditions, as shown in Fig. 1b, the differences between this 'baseline' cathodic current ($I_{c,\text{Lim}}$) and the cathodic current density supplied to each specific electrode in order to polarize them to E_{CP} (i.e. I_A , I_B or I_C), can be attributed to the anodic current density at each particular electrode (i.e. $I_{a,\text{CP-A}}$, $I_{a,\text{CP-B}}$ or $I_{a,\text{CP-C}}$). Subsequently these anodic current densities can be used to calculate the local corrosion rates.

Conversely, the value of $I_{c,\text{Lim}}$ can be obtained using an inert metal electrode or be estimated by adopting the value of the largest cathodic current measured using the array (represented by electrode C in Fig. 1b, i.e. I_C). This takes advantage of the fact that as the anodic current at that electrode ($I_{a,\text{CP-C}}$) approaches zero, the current measured at the same electrode (I_C) approaches $I_{c,\text{Lim}}$. This estimation method assumes that only negligible anodic current densities ($I_{a,\text{CP-C}}$) are present at the most cathodic electrode. Electrodes at the edges of the array are not considered in this analysis due to their different accessibility to oxygen.

Material and Methods

Figure 2 shows the experimental setup used to assess the method described above. A 2.5 L electrochemical cell was used to establish a simple experimental condition. The 0.1 M NaCl test solution was prepared from analytical grade reagents and ultrapure ASTM D1193 type 1 water (pH 6). The solution was aerated overnight and was left open to air during the test. The electrode array¹³⁻¹⁵ consisted of one hundred 1.6 mm diameter UNS G10350 steel wires arranged in a 10 by 10 square array of 18.5 mm in length. The wires were mounted in epoxy resin and equally spaced at a distance of approximately 0.27 mm. The array surface was abraded with silicon carbide papers to 1200 grit finished using water as a lubricant, and then rinsed with ethanol and acetone. Tests were performed in duplicate at a temperature of 22°C. A Zero Resistance Ammeter (ZRA 1) was used to measure local current flowing to (or from) any selected electrode in the array by connecting the ZRA1 between the selected electrode and the remaining 99 electrodes. The electrode array connections were managed by an automatic switcher (switching once every 10 seconds). In this way, current distributions over the whole electrode array are measured by completing a scan every 20 min.

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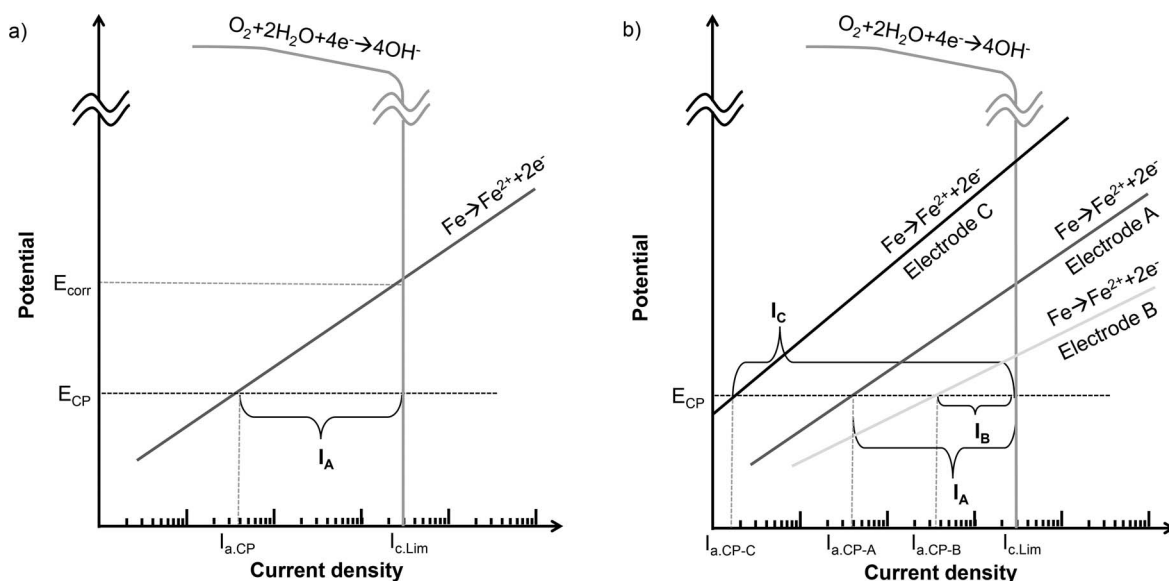


Figure 1. Schematic Evan's Diagrams illustrating the theoretical basis for the proposed method. Single electrode case (a). Multi-electrode case (b).

A 1 mm diameter, 11.6 mm long platinum electrode was also exposed to the same solution and maintained at the same potential. The net current flowing through this electrode (I_{Pt}) was measured by a second ZRA (ZRA2). The platinum electrode was used to measure the 'baseline cathodic current density' that is considered to be the limiting current density for the diffusion controlled cathodic reaction. A constant -760 mV CP potential against a Ag/AgCl (Sat. KCl) reference electrode (Ref. in Fig. 2) was achieved by applying the CP current (I_{CP}) using a potentiostat. The counter electrodes (CE in Fig. 2) were two 4.5 mm diameter graphite rods with 120 mm immersed in the solution. The currents obtained by ZRA1 were used to construct current density distribution maps using a script designed for Matlab 2012b. At the end of each test, the array was removed from the cell, rinsed with ethanol and acetone and photographed. The array was then placed back into the cell where the solution was replaced by a NaOH solution (pH 12) for cathodic cleaning. After cleaning, the array was rinsed with ethanol and acetone again. The large size of the WBE made the direct analysis of its surface difficult; therefore a replica of the corroded surface was obtained using a silicone based replica kit. A Wyko NT9100 Interferometry Profilometer was used to evaluate

the severity of the attack over the surface replica. The volume of the pits was calculated based on the profilometry data using the software Vision V3.60.

Results and Discussion

The current densities measured by the electrode array were used to generate surface maps by using linear interpolation. A typical map is presented in Figure 3 (A video showing dynamic changes of current densities is presented as a supplementary material to this Letter). A characteristic feature that is observable in Figure 3 (and also in the video) is that a generally constant 'baseline' cathodic current existed for most of the electrodes in the array, forming a 'platform' in the current density distribution maps. This baseline cathodic current value is believed to be the cathodic limiting current density ($I_{c,Lim}$). In the same figure, it is also observable that some particular electrodes presented significantly lower cathodic current densities. As described in the theory section, these electrodes with significantly lower cathodic current densities can be explained by the presence of anodic reactions occurring at them. Furthermore, the difference between the cathodic current measured at each electrode and the 'baseline' cathodic current can be used to determine the local anodic corrosion rates. Subsequently, successive local corrosion rate measurements can be

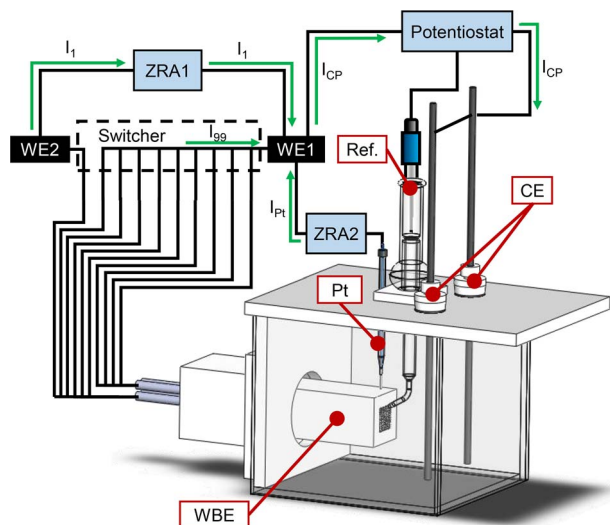


Figure 2. Schematic representation of the electrochemical cell and instrumentation used.

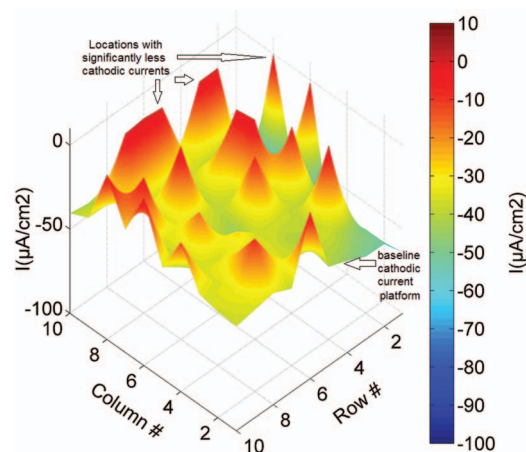


Figure 3. Typical current density distribution map obtained during immersion test in 0.1M NaCl at -760 mV_{Ag/AgCl}.

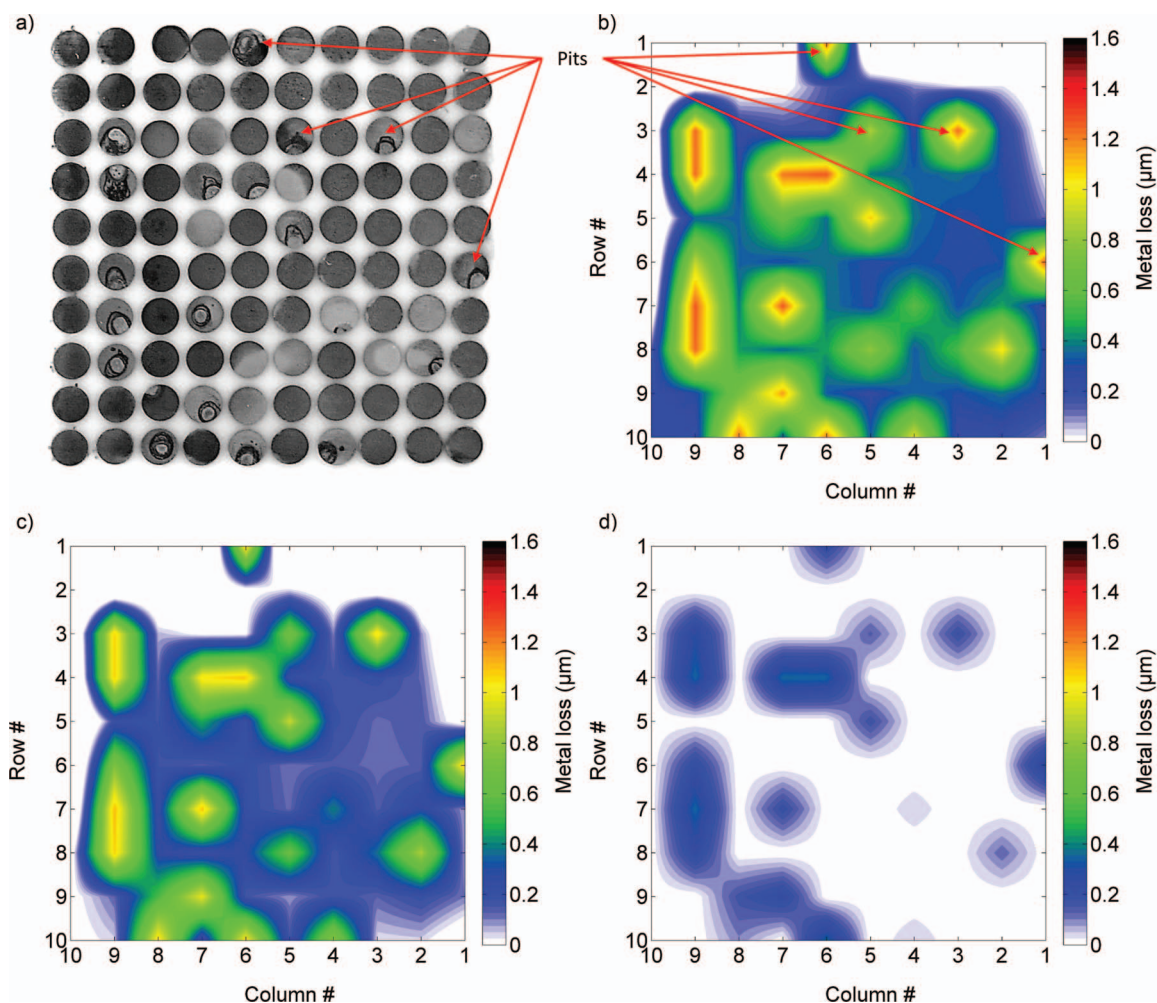


Figure 4. Comparison between the array surface after 23 h immersion in 0.1 M NaCl at $-760 \text{ mV}_{\text{Ag/AgCl}}$ and calculated results from electrochemical methods. Photograph of the array (a). Metal losses calculated using current Pt electrode data as baseline cathodic current (b). Metal losses calculated using the largest cathodic current registered by the array as baseline cathodic current (c). Metal losses from surface profilometry measurement results (d).

used to determine metal loss and its distribution based on Faraday's law.

If the method described above correctly measures corrosion under CP, a correlation between actual and calculated metal losses should be achievable after a certain period of exposure. Figures 4a–4d present the results of such comparison. It is clearly shown that a very high correlation was obtained between actual (Fig. 4a) and calculated (Fig. 4b and 4c) corrosion patterns. When comparing the results calculated based on the different methods used to determine the cathodic limiting current (Fig. 4b and 4c), it was found that metal losses values were approximately 10% ($0.17 \mu\text{m}$) higher for the Pt electrode case (Fig. 4b). This difference may suggest that a small anodic current existed on the electrode that registered the largest cathodic current on the array, causing the generalized underestimation of metal losses presented in Figure 4c. Nevertheless in this experiment the error due to these factors has been relatively small, suggesting that the largest cathodic current registered by the array could effectively be used to determine the baseline cathodic current value for corrosion calculations, lessening the need for an extra inert metal electrode.

Surface profilometry was used to measure pit depths and to estimate mass losses for all electrodes in the corroded array. In order to establish a direct comparison with metal loss maps calculated from electrochemical data, the volume of the pits found at each electrode was divided by the nominal area of one electrode. The results of such calculations for all significantly pitted electrodes are presented in Figure 4d in a metal loss map. The metal losses distribution obtained

by profilometry (Fig. 4d) is in reasonable agreement with that measured electrochemically (Fig. 4b and Fig. 4c), although the magnitude of the metal losses determined by profilometry is generally lower. Possible reasons for this discrepancy that might have induced some error in the determination of the pits volume are under further investigation (effectiveness of the corrosion products cleaning method, initial surface roughness and the accuracy of the surface replica). Nevertheless the correlation between actual and calculated corrosion metal losses demonstrates the capabilities of the new method for measuring localized corrosion and its distribution under CP. This unique capability could potentially lead to new research as well as industrially oriented practical applications. For instance, this measurement principle could be used to study the influence of the CP potential on the inhibition and distribution of local corrosion sites or how dynamic fluctuations in the CP potential could affect the corrosion behavior of a given alloy. From an industrial point of view, this measurement principle could be the starting point for the development of new corrosion monitoring tools capable of performing electrochemical measurements under CP.

Conclusions

A new method to estimate corrosion rates and their distribution from current distribution measurements using an electrode array under CP has been presented. The method is applicable to systems in which the main cathodic reaction rate is diffusion controlled and does not require CP interruption to perform electrochemical measurements.

The oxygen limiting current was used as a baseline value for the estimation of anodic currents under CP. This baseline value was measured using an inert Pt electrode as well as the electrode array obtaining similar results. The accuracy of this new analysis method has been assessed by comparing calculated metal loss maps with visual inspection and surface profilometry results of the attacked array surface. In general, a good correlation between calculated and actual metal loss was found.

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