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Electrochemical determination of rusted steel surface stability

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The stability of a rusted steel surface exposed to a 0.1 M sodium sulphate solution has been studied. Electrochemical impedance spectroscopy, polarization resistance and atomic absorption analysis techniques were used in conjunction with mild steel specimens rusted in a rural atmosphere and treated with different concentrations of phosphoric acid. Since most of the impedance diagrams obtained differ from the typical semicircle, it is not clear how to obtain kinetic information on the corrosion process. The polarization resistance technique gives more useful data.

1. Introduction

As is already known [1–3], the electrochemical reduction and oxidation reactions that take place between rust and a steel substrate are greatly detrimental to the anticorrosive behaviour of organic coatings, even if these coatings are hypothetically tolerant to rusted surfaces.

In this paper the possibility of obtaining information about the stability of rusted steel exposed to an electrolyte by means of a.c. and d.c. electrochemical measurements is studied. The response of electrodes covered with corrosion products and, more specifically, the response of steel covered by porous oxidic layers to electrical signals has been considered in a number of papers [4–11]. However, in the case of prerusted steel a complicated situation arises, in which many interacting factors may contribute to the kinetics of the system [1–3, 9, 11, 12].

2. Experimental details

Mild steel plates were rusted for two years in a pollution-free rural atmosphere. The rust layer of about 23.1 mg cm^{-2} of exposed surface was treated with phosphoric acid. For this purpose, 0.2 ml of the phosphoric acid solution was spread over 10 cm^2 of rusted surface by means of a pipette. The steel specimens thus treated were stored in a desiccator for at least 2 days before testing.

Later, the test pieces were immersed for different periods of time in a 0.1 M sodium sulphate solution. The amount of iron passing into this solution gave a measure of the rusted steel stability. For these tests the edges and the back face of the test pieces were protected with wax, leaving exposed to the saline solution a 9 cm^2 surface area. The analysis of the dissolved iron in the saline solution was carried out by atomic absorption. In order to determine the effect of the exposure period, the amount of iron passing into the solution between days 1 to 3, 7 to 9, and 13 to 16 after exposure to the sodium sulphate solution was measured. All these tests were carried out in duplicate.

The classic three-electrode technique was used for the electrochemical tests. The rusted steel surface area (working electrode) was limited by using a short piece of glass tube placed on the specimen. The system is basically similar to that used by other authors [13, 14]. The glass tube contained electrolyte, and the reference and counter electrodes. The surface area of the rusted steel exposed to the electrolyte was 6 cm^2. All these electrochemical tests were performed in the vicinity of the rest potential.

The a.c. tests were carried out with the help of a Solartron 1250/1286 instrument. A sinusoidal signal of 10 mV (r.m.s.) was applied over the frequency range 15 kHz to 1 mHz. In the d.c. tests a potential step of ± 10 mV was applied and the current response was measured. In general, good reproducibility was obtained for the impedance diagrams as well as for the polarization resistance determinations.

The Stern–Geary equation was used to calculate the corrosion intensity (I_{corr}):

$$I_{\text{corr}} = B/R_{\text{p}}$$

where R_{p} is the polarization resistance and B is a constant which contains Tafel slope information [15].

3. Results and discussion

3.1. *Nyquist diagrams*

Figure 1 represents the different types of impedance diagrams obtained for the rusted steel test pieces. Type I appeared with rusted steel without treatment, while Type II was observed with rusted steel treated with phosphoric acid of 15% concentration or higher. The Type III appeared in the treatment of rusted steel with

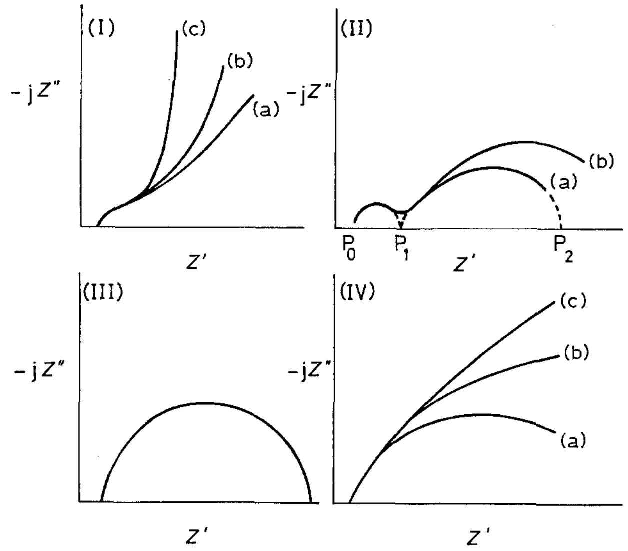

Fig. 1. Impedance diagram types obtained with rusted steel in the frequency range 55 kHz to 1 mHz.

phosphoric acid of about 30% concentration, and Type IV with rusted steel treated with phosphoric acid of different concentrations but after long periods of time of exposure to the saline medium. The Types II and III tended to change with time towards Type IV.

In general, the difference between Z'_0 and Z'_∞ (real parts of the impedance vector at $\omega \longrightarrow 0$ and $\omega \longrightarrow \infty$, respectively) can be used to obtain kinetic information in the same way as the value of R_p obtained with the d.c. Nevertheless, with the rusted steel it is doubtful if the value of Z'_0–Z'_∞ is determined by the charge transfer resistance (R_T) of the corrosion process (which is the magnitude that should really be used in the Stern–Geary equation to estimate the corrosion rate).

A region is often found in which the Z' (real part of impedance) and Z'' (imaginary part of impedance) values are approximately proportional to $\omega^{-1/2}$ (Fig. 2). This behaviour may arise from semi-infinite diffusion conditions, which are possible over a certain frequency range, provided that the a.c. diffusion layer is much smaller in dimension than the diffusion layer. At sufficiently low frequencies, diffusion begins to be limited by the finite length of the diffusion layer, and the low frequency tail tends to curve towards the real axis if the far end of the diffusion region corresponds to a transmissive boundary, or to curve upwards (slopes above 45°) if it corresponds to a reflective boundary [16]. The latter tail form is typical of many solid electrolytes, and it may also be shown by the rust layer. In fact, deviations from the 45° line may also occur, even under semi-infinite conditions, as a result of the parallel combination of the cathodic and anodic contributions to the electrical signal response. On the other hand, a porous electrode can also have a frequency response with similar features [17, 18]. The fact that the rust has a certain degree of electronic conductivity can favour its performance as a porous electrode.

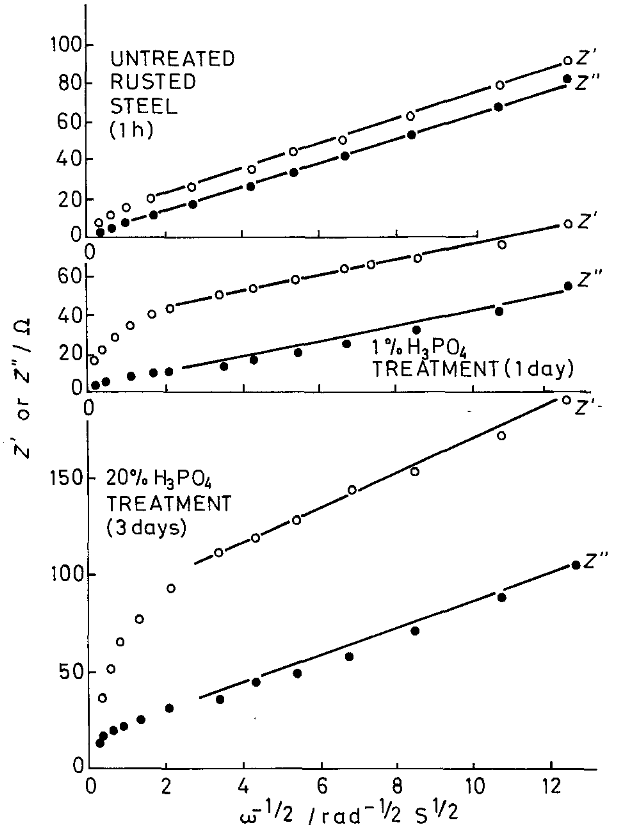

Fig. 2. Representation of the impedance (Z' and Z'') against $\omega^{-1/2}$.

A serious practical problem for the interpretation of the impedance diagrams for rusted steel is that many of these diagrams are far from complete at the lowest of the tested frequencies (1 mHz), making it impossible to determine Z'_0 from the intercept with the real axis. This occurs principally with the Type I and Type IV diagrams (curves b and c) in Fig. 1. Of the four types of diagrams, the only ones that permit a clear determination of the R_T value are those of Type III, in which R_T is identified with the semicircle diameter. In this case there should be no doubt about the electrochemical estimation of the corrosion rate. It is possible that the charge transfer reaction, diffusion processes and the porous nature of the electrode jointly participate in the form of the remaining diagrams (Types I, II and IV).

3.2 *D.c. signal responses*

As in the a.c. data, two types of problems now appear: a practical one related to the procedure, and a theoretical one, related to the interpretation of the results. The former is due to the fact that the current response, ΔI, to the application of a potential step, ΔE, does not stabilize with time; the value of ΔI decreases continuously, even after several minutes of measurement.

In theory, the value of R_p should be determined when the system response to the potential step reaches a steady state, usually in a fraction of a second. If the relaxation time of the system is very long, however, it may not reach such a state. This happens with rusted steel; a strong time dependency of the current response is observed. In these cases, prolonged d.c. polarization can change the corrosion potential during measurement, introducing an additional error into the R_p

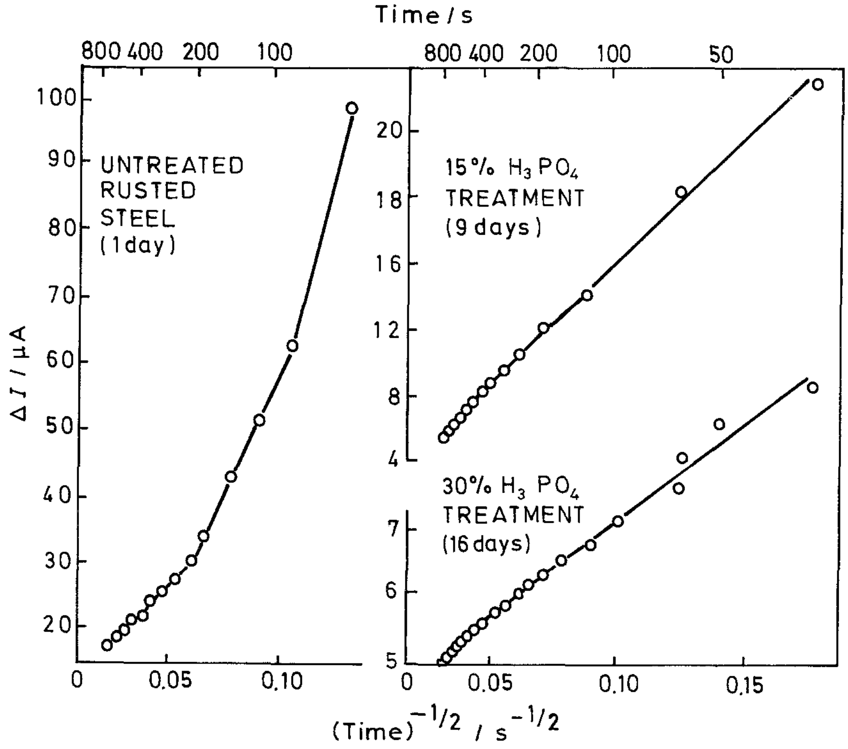

Fig. 3. Representation of the current response (ΔI) against $t^{-1/2}$.

determinations. Thus, it is necessary to extend the polarization application time in order to approach the steady state but this time cannot be extended excessively because of the probability that other undesirable effects disturb the determination (spontaneous changes in E_{corr}). For this reason, an intermediate time interval is selected empirically, even though this means taking measurements under non-steady conditions, with a value of R_p that involves some error.

On the other side, it is unlikely that the R_p value measured with rusted steel is a function only of electrochemical reaction rates (to which the Stern–Geary equation apply) and is not affected by diffusion processes. In the case of a diffusion controlled electrode reaction, the response in current (ΔI) to a potential step decreases with time (t), and a relation of the type

$$\Delta I \propto t^{-1/2}$$

is verified over a large time interval before reaching steady state [19]. Relations of this type are found with rusted steel (Fig. 3). Under these conditions, in which diffusion plays a significant role in the kinetics of the process, the Stern–Geary equation is not exactly applicable. Even so, the experimental results indicate the possibility of an approximate assessment of the corrosion current, as will be discussed below.

3.3 *Comparison between electrochemical estimations and analytical determinations*

The amount of iron dissolution (Table 1) has been used to calculate the polarization resistance corresponding to the corrosive process, supposing that the Stern–Geary equation is applicable with a value of B of 26 mV. This resistance is designated R_a in order to differentiate it from the R_p, obtained directly by using the d.c. signal. Figure 4 shows a typical example of the relative order of R_p values (determined after 4 min of polarization) and of R_a and Z' (real part of the impedance) values obtained in rusted steel. The values of R_p and R_a are comparable and are much higher (e.g., 6–12 times) than the value of Z' obtained with the a.c. method at the smallest frequencies applied (i.e. 1 mHz). The form of the impedance diagram does not influence the result. Although in Fig. 4 the value of R_a is greater than the value of R_p, the opposite situation is also possible in other cases.

The similarity between the values of R_p (determined with the d.c.) and R_a supports the possibility of estimating the corrosion rate by electrochemical measurements. However, the excessively low value of Z' at 1 mHz disqualifies the a.c. method for these determinations. The enormous difference between the Z' value at 1 mHz and R_p is attributed to the fact that many of the diagrams are still far from completion at this frequency [20].

Table 1. Mean corrosion rates of rusted steel (mg cm^{-2} d^{-1}) for different treatments and exposure times to a 0.1 M sodium sulphate solution

Rust treatment	*Exposure time*		
	1–3 days	*7–9 days*	*13–16 days*
Untreated	0.16	0.15	0.14
With 5% phosphoric acid	0.08	0.08	0.10
With 15% phosphoric acid	0.19	0.06	0.06
With 30% phosphoric acid	0.41	0.04	0.05

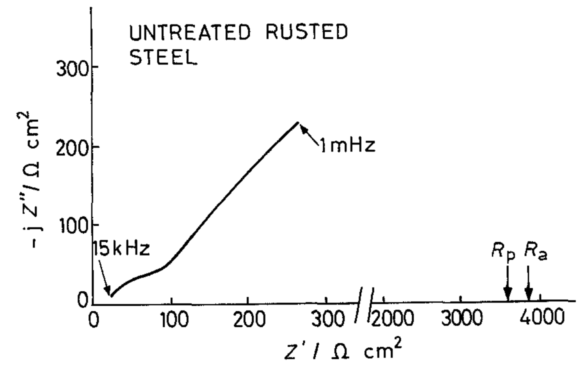

Fig. 4. Comparison of R_p, R_a, Z' and Z'' values obtained with the rusted steel/electrolyte system.

In Table 2, the corrosion rate data obtained by chemical analysis (expressed as I_{corr}) are compared with the values of R_p for identical treatments and exposure times to the sodium sulphate solution. The value of the relation I_{corr}/R_p will coincide with the value for the B constant in the assumption that a similar equation to that of Stern–Geary is fulfilled. On the basis of the values given in Table 2, an average value of B of 16.8 mV is deduced in the case that the apparent R_p values are determined after 4 min of polarization, and an average value of B of 27.5 mV if these values are determined after 8 min. At a 95% confidence level, the electrochemical estimation error is around 100% using the analytical data as indicator. Therefore, it is not possible to obtain a precise electrochemical determination of the corrosion rate. This result was foreseeable in view of the reasons offered in the preceding discussion.

4. Conclusions

(i) The complexity of the processes influencing the electrochemical behaviour of the rusted steel/electrolyte system (in which diffusion processes and the electrode's porous nature seem to play an important role) hinders a precise determination of the corrosion rate by means of a.c. and d.c. electrochemical measurements.

(ii) The majority of the Nyquist diagrams obtained with the rusted steel deviate from the typical semicircular form. For this reason, it is not clear how kinetic information can be obtained from these diagrams and the Stern–Geary equation. A further difficulty is that, even at 1 mHz, these diagrams usually have an important capacitative component that makes uncertain the extrapolation to the real axis.

(iii) It therefore seems preferable to use the d.c. data for the electrochemical determination of the corrosion rate for rusted steel. Nevertheless, with d.c. the stationary state is not reached even after several minutes of application of the polarizing potential, and it is thus necessary to use apparent values of the polarization resistance (R_p) in the Stern–Geary equation.

(iv) These values of R_p are verified to have an approximately inverse proportion to the quantity of iron ion that passes to the saline medium. It is

Table 2. Corrosion current densities (I_{corr}, μm cm^{-2}), calculated from analytical data, and apparent polarization resistance values (R_p, Ω cm^2), from electrochemical measurements made 4 and 8 minutes after application of the polarizing potential

	Rust treatment		*Exposure time*			
	1–3 days		*7–9 days*		*13–16 days*	
	I_{corr}	R_p	I_{corr}	R_p	I_{corr}	R_p
Untreated	6.61	(4 min) 3700	6.20	(4 min) 3494	5.78	(4 min) 2735
		(8 min) 6290		(8 min) 6910		(8 min) 7863
With 5% phosphoric acid	3.30	(4 min) 2419	3.30	(4 min) 2516	4.13	(4 min) 2995
		(8 min) 4600		(8 min) 3494		(8 min) 5242
With 15% phosphoric acid	7.85	(4 min) 2995	2.48	(4 min) 3700	2.48	(4 min) 3931
		(8 min) 5540		(8 min) 6290		(8 min) 6989
With 30% phosphoric acid	16.9	(4 min) 2621	1.65	(4 min) 5718	2.07	(4 min) 6990
		(8 min) 3220		(8 min) 7450		(8 min) 8986

therefore possible to use a similar equation to Stern–Geary's for a rough estimation of the corrosion rate in the rusted steel/electrolyte system.

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