

Measurement of Accumulated Corrosion and Instant Corrosion Rate Using a New Differential Electrical –Resistance Technique

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Abstract

This paper describes the theoretical background and preliminary test results from an investigation in which the instant corrosion rates and accumulated corrosion of steel exposed in an acetic acid buffer solution has been measured on the same metal element by means of a new ER-technique in which the changes of the electrical resistance of a steel foil mounted on a printed circuit board has been measured. The measurement can be made with an accuracy of $0.1 \mu\Omega$, which means that e.g. a corrosion rate of $20 \mu\text{m}/\text{year}$ can be detected within few minutes. The concept was tested by following the time changes of the resistance during a potential scan. It is shown that the ER measurement performed excellent in detecting changes in the corrosion mode (cathodic protection, active corrosion and passivity). In addition, the instant corrosion rate measured by the ER-technique is compared with the corrosion rate calculated from applied anodic current densities showing a very precise linear correlation. Additionally, a linear correlation was shown between coupon resistance and temperature suggesting that the measurement can be used to estimate the temperature as well.

The technique seems to be very promising and applicable in a range of corrosion studies in the laboratory as well as for monitoring purposes. In particular, the concept may be used in cases where the corrosion cannot be quantified by simple electrochemical means (atmospheric corrosion, corrosion of reinforcement in concrete, AC induced corrosion, corrosion under insulation, microbial corrosion in sulphide environments, etc.).

1. Introduction

Several techniques exist that can be used for quantification of instant corrosion rates as well as accumulated corrosion. Instant corrosion rates are normally measured by means of electrochemical techniques like electrochemical impedance spectroscopy (EIS), linear polarisation resistance (LPR) measurements, or electrochemical noise (EN), etc. These techniques are believed to be non-destructive to the metal surface, however, the EIS and LPR techniques have in common the need to polarise the metal and measuring e.g. the current response to a small potential perturbation. This means that the electrochemical processes occurring at the metal surface are accelerated and studied in a (narrow) region around the open circuit corrosion potential (OCP). Since the metal is polarised, it cannot be excluded that the metal surface is damaged in the sense that the surface does not behave during the measurement as if no polarisation was made. In addition, current response from redox-processes other than those involved in the corrosion process affects the accuracy of the measurement. The EN technique may provide a measure of the instant corrosion rate without polarising the metal surface, but it requires expensive and advanced electronic hardware as well as expertise when it comes to interpretation of the test results. The Tafel polarisation technique can be used for measurement of the instant corrosion rate as well, but his technique is definitely destructive since the method involves a large polarisation of the metal. Therefore, the technique cannot be used for real time corrosion monitoring.

As a general rule of thumb, the low-potential perturbation techniques (EIS, LPR,) may determine the corrosion rate with accuracy within a factor 2.

Accumulated corrosion can be quantified e.g. by weight loss measurements, ultrasonic based thickness measurements, and general visual investigations (microscopy). In addition, measurement of the electrical resistance in a corroding metal wire placed in a probe designed for this purpose (the ER technique) is a very common way of monitoring the accumulated corrosion in process plants. The techniques applied for determination of accumulated corrosion have in common that they require some time before the degree of corrosion is sufficiently high to be detected by these techniques. By following the accumulated corrosion throughout an extended period of time, the average corrosion rate throughout this period can be calculated. Instant corrosion rates cannot be measured by any of these techniques, though it is recognised that thin metal elements (100 μm thickness) have been successfully incorporated in commercial ER-probes and applied in process plants to follow the efficiency of corrosion inhibitor dosage with a fairly quick response (days).¹

The present paper describes preliminary test results from an investigation in which the instant corrosion rates and accumulated corrosion has been measured on the same metal element by means of a new technique based on the ER-concept.

2. The ER-technique – theoretical considerations

In general, the ER-technique utilises that the electrical resistance in a metal plate increases when the plate suffers from metal loss due to corrosion.

Considering a metal plate with dimensions as illustrated in figure 1, the electrical resistance of the plate (as a function of plate thickness, σ , and temperature, T) can be described by:

$$R(T, \sigma) = \rho(T) \cdot \frac{L}{W \cdot \sigma} \quad (1)$$

where $\rho(T)$ is the electrical resistivity of the metal.

The electrical resistivity of a metal depends strongly on the temperature. As an example, literature data for pure iron are presented graphically in figure 2 (broad temperature range) and figure 3 (0-130°C).² As observed from these figures, the resistivity does not depend linearly on the temperature throughout the broad temperature range (figure 2), whereas a linear dependency can be approximated in the temperature range 0-130°C (figure 3). The Approximation can be expressed as:

$$\rho(T) = aT + b \quad (2)$$

where $a = 0.0601$, and $b = 8.4341$.

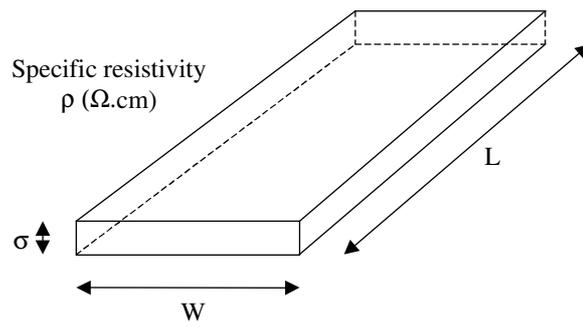


Figure 1. Schematic illustration of dimensions of metal plate used in calculations of electrical resistance according to equation (1).

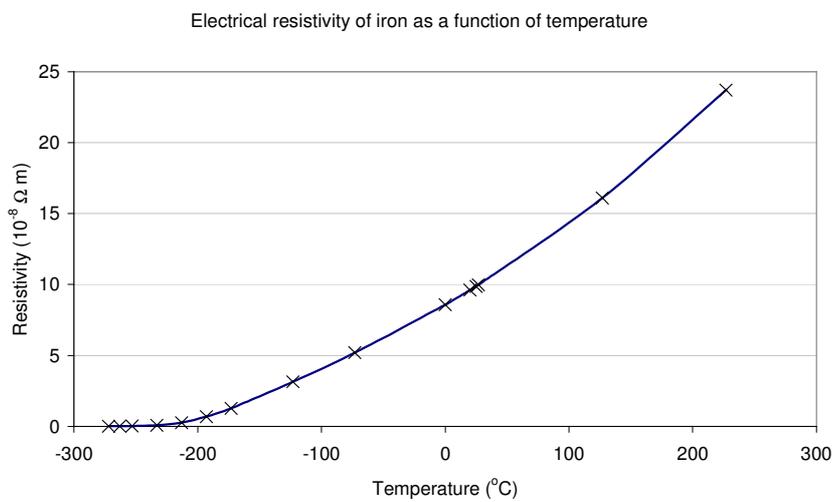


Figure 2. Resistivity of pure iron as a function of temperature (broad range).²

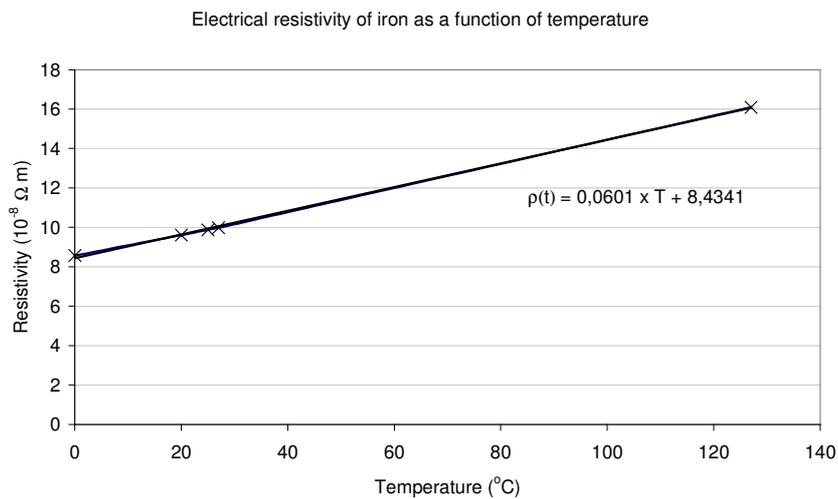


Figure 3. Resistivity of pure iron as a function of temperature (0-130 °C).²

By inserting equation (2) into (1), the resistance of a metal plate in the temperature range leading to a linear resistivity-temperature dependency can be calculated by:

$$R(T, \sigma) = (a \cdot T + b) \cdot \frac{L}{W \cdot \sigma} \quad (3)$$

At constant plate length (L), plate width (W), and temperature (t), the resistance of the plate as a function of the plate thickness (σ) can be simplified into:

$$R(\sigma) = \frac{K}{\sigma} \quad (4)$$

where the constant K includes the specific resistivity and the plate dimensions apart from the thickness σ .

The general corrosion rate of the metal plate can be expressed by the rate of reduction of the plate thickness:

$$V_{\text{corr}} = -\frac{d\sigma}{dt} = -\frac{\frac{dR}{dt}}{\frac{dR}{d\sigma}} \quad (5)$$

It follows from equation (5) that by measuring dR/dt the corrosion rate can be estimated if $dR/d\sigma$ is known. Differentiating equation (4) gives:

$$\frac{dR}{d\sigma} = \frac{-K}{\sigma^2} = \frac{-R^2}{K} \quad (6)$$

It follows that:

$$V_{\text{corr}} = \frac{dR}{dt} \cdot \frac{K}{R^2} \quad (7)$$

where

$$K = (a \cdot T + b) \cdot \frac{L}{W} \quad (8)$$

In conclusion, the corrosion rate of the metal plate can be estimated by measuring co-ordinate values of dR/dt and R. The temperature has to be known as well.

3. Probe- and instrument design

A probe based on a thin steel foil placed on a printed circuit board (PCB) was designed and manufactured for the purpose of being able to measure co-ordinate values of dR/dt and R throughout time during an experiment in which the foil was

corroding under controlled conditions. A sketch of the probe design is given in figure 4.

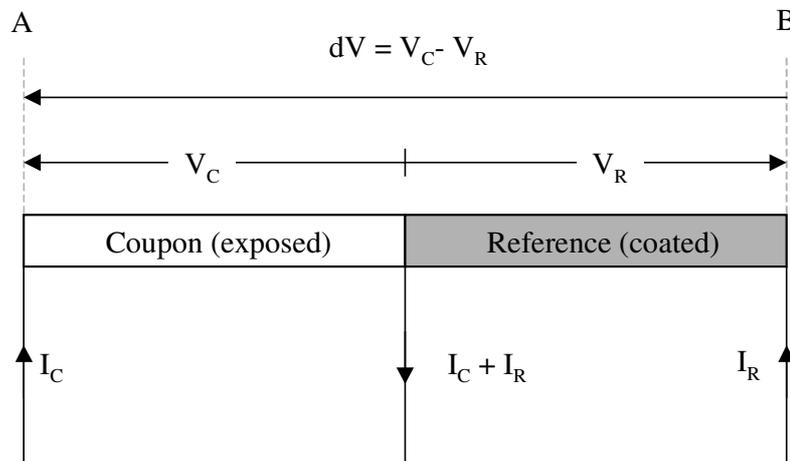


Figure 4. Schematic illustration of the ER-probe design.

The foil was coated at half its length in order to protect this part of the foil from corrosion (designated “reference”). The other part of the foil was exposed in the corrosive environment (designated “coupon”). Electrical connections positioned at each end and in the middle of the foil were provided by copper conductors fabricated in the PCB by the photo-resist technique.

An instrument (micro-ohmmeter, figure 5) was designed and manufactured which is able to pass specific AC-excitation currents (0.25 A, 1000 Hz) through the coupon as well as through the reference. Measuring the voltage drops V_C and V_R , the coupon and the reference resistance can be quantified individually by dividing by the excitation current.



Figure 5. Photograph of the micro-ohmmeter.

Measuring the voltage drop between the points A and B in figure 4, the difference dR between coupon and reference resistance can be quantified. Prior to exposure to the

corrosive environment, the reference and the coupon resistance are equal, and during the corrosion process, the resistance of the coupon increases. Accordingly, the reduction in thickness of the coupon can be quantified by dV divided by the excitation current, i.e. dR . By measuring dR with sufficient accuracy throughout time, dR/dt can be registered within short time intervals and used to determine the instant corrosion rate according to equation 7. The resolution of the micro-ohmmeter is $0.1 \mu\Omega$.

The dimensions of the coupon and the reference used in the present investigation were $L = 87.0 \text{ mm}$, $W = 9.7 \text{ mm}$, and $\sigma = 0.025 \text{ mm}$. The iron content of the foil was 99.5 %. Using these dimensions and the literature data for pure iron regarding the specific resistivity as a function of the temperature, the theoretical (expected) foil resistance can be calculated according to equation (3), and the outcome of this calculation shown graphically in figure 6.

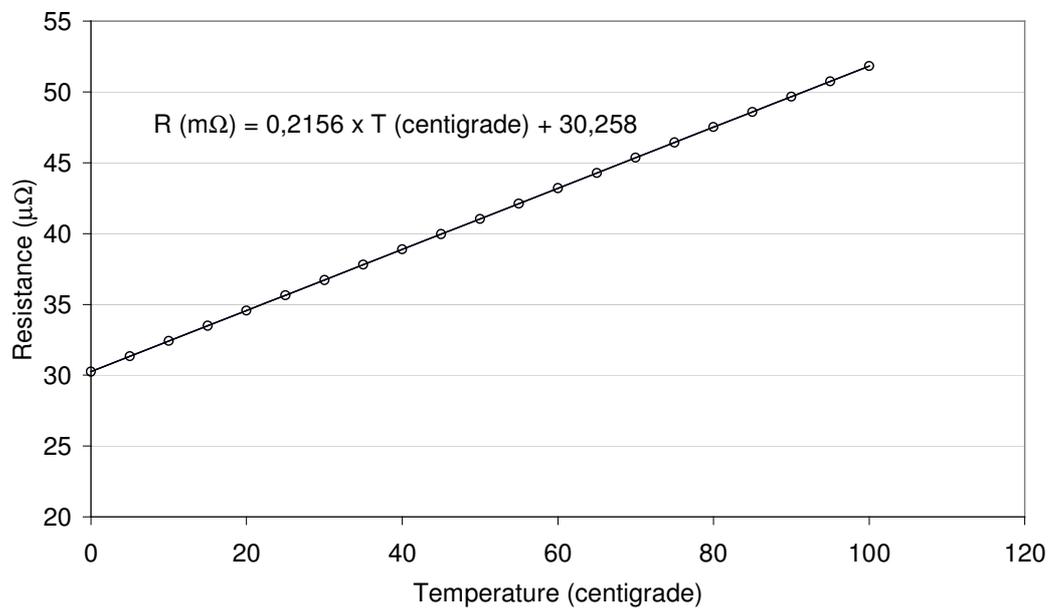


Figure 6. Theoretical dependency of iron coupon resistance on temperature.

A fit of the data in figure 6 gives the following relation between coupon resistance and temperature:

$$R(\text{m}\Omega) = 0.2156T (\text{°C}) + 30.258 \quad (9)$$

Figure 7 shows the theoretical coupon resistance as a function of coupon thickness at 20°C (calculated from equation (7)), and figure 8 shows the theoretical relation at 20°C between instant corrosion rate and dR/dt , assuming that the coupon resistance is constant during the measurement (the measurement is made within a short period of time and the reduction of the coupon thickness can be disregarded within this period).

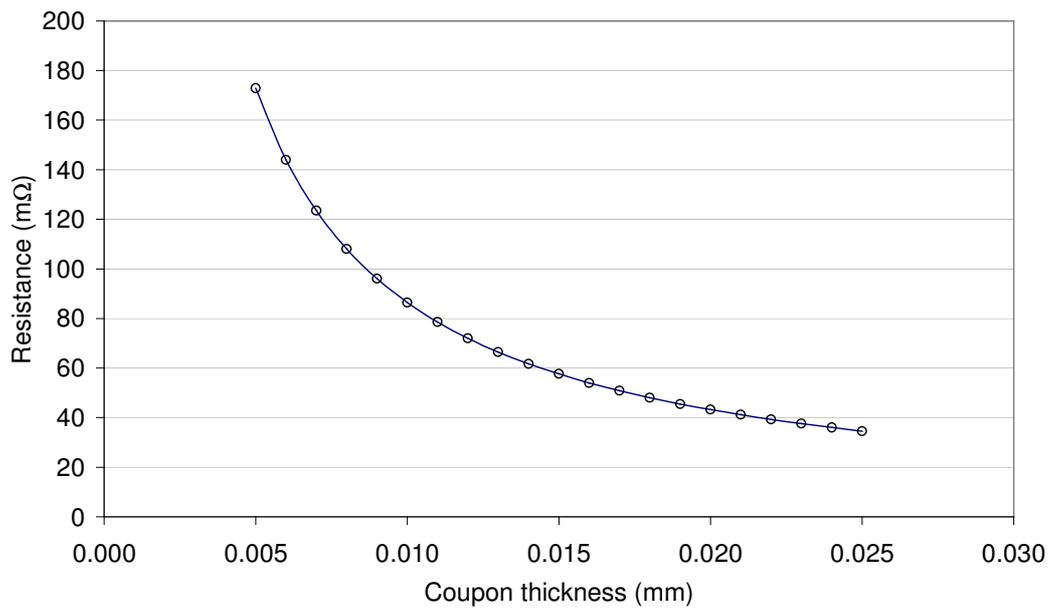


Figure 7. Theoretical coupon resistance as a function of coupon thickness at 20 °C.

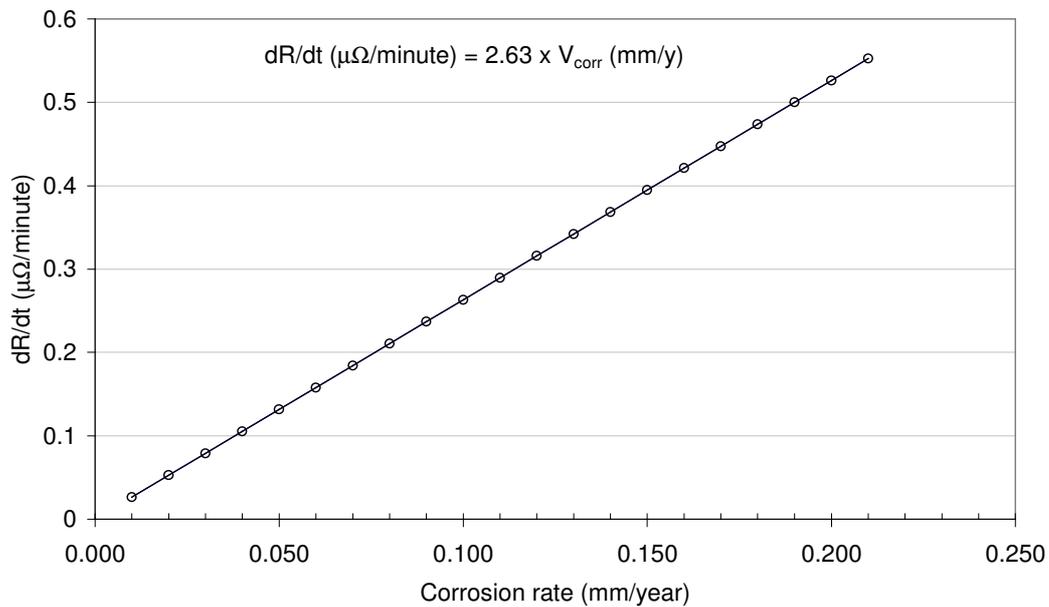


Figure 8. dR/dt as a function of the corrosion rate (theoretical) at 20 °C.

The data in figure 8 gives the following correlation between corrosion rate and dR/dt at 20°C:

$$V_{\text{corr}} \text{ (mm/y)} = 0.38 \cdot \frac{dR}{dt} \text{ (}\mu\Omega/\text{minute)} \quad (10)$$

With reference to the above figures 6-8, it is clear that two major challenges that have to be overcome are:

1. The measurement has to be very sensitive in order to make a quick measurement, otherwise the coupon resistance changes too much (figure 7) before a corrosion rate is determined, and the theoretical mathematical basis for the corrosion rate calculation becomes invalid. The resolution of the present micro-ohmmeter is $0.1 \mu\Omega$, which means that a corrosion rate of e.g. $20 \mu\text{m}/\text{year}$ can be detected within a few minutes (figure 8 and equation (10)). Within 10 minutes at this corrosion rate, the coupon resistance changes approximately $0.5 \mu\Omega$.
2. Since low corrosion rates (e.g. $20 \mu\text{m}/\text{year}$) requires that very low changes of the coupon resistance can be measured, it is absolutely necessary that the temperature is constant during the measurement on both the coupon and the reference foil. As noted from figure 6 and equation (9), a temperature change of 1°C results in a resistance change in the region of $215 \mu\Omega$. This means that the excitation current provided by the micro-ohmmeter in itself may change the resistance of the coupon and reference foil to an extent that far exceeds the resistance change (dR) that has to be measured for the purpose of detecting the corrosion rate. Further, the inductive loops resulting from the AC excitation current passed in the electrical circuit may introduce imaginary impedance that eventually may influence the accuracy of the measurement.

The huge temperature effect on the ER-measurement is overcome by the present technique by making the differential measurement as illustrated in figure 4. The coupon and the reference are part of the same foil, hence, a temperature difference is levelled out via the thermal conductivity of the foil. Further, the instrument is equipped with a balance facility, which (while the excitation current flows) levels out the difference in resistive impedance between the coupon and the reference. In addition, a second balance facility ensures that differences in inductive impedance (caused by the AC excitation current) between the coupon and the reference is levelled out prior to the measurement.

In conclusion to the above, the design of the ER-probe and the micro-ohmmeter allows for measurement of the accumulated corrosion by measuring the absolute resistance of the coupon and reference separately, and for detecting the instant corrosion rate by applying the differential technique. In the latter case, any difference in the initial real part as well as imaginary part impedance of the coupon and reference is levelled out by balance facilities included in the instrument. This ensures that at time = 0, dR is adjusted to zero regardless of the actual difference in absolute resistance. Hereafter, the change in dR due to corrosion can be measured throughout time.

4. Experimental

Studies on the temperature effect on absolute resistance of coupon.

Initially, the effect of temperature on coupon resistance was studied by placing the ER-coupon into a glass vessel containing ethanol (to avoid corrosion of the coupon).

The vessel was immersed into a thermostat bath, and the coupon resistance measured in the temperature range 30-55°C using intervals of 5°C.

Correlation between a DC-polarisation scan and dR/dt .

Secondly, the performance of the dR measurement was tested. This was made by establishing a traditional three-electrode electrochemical cell in which the exposed coupon acted as the working electrode, a saturated calomel electrode placed in a Luggin capillary acted as reference, and a titanium mesh was used as counter electrode. The test was conducted in a 0.1 M NaAc/Hac buffer at pH 6 with free air access at ambient temperature ($\cong 20^\circ\text{C}$). A potentiostat and a scanner (Wenking laboratory models) were used to control the potential of the exposed coupon. A photograph of the test set-up is presented in figure 9.

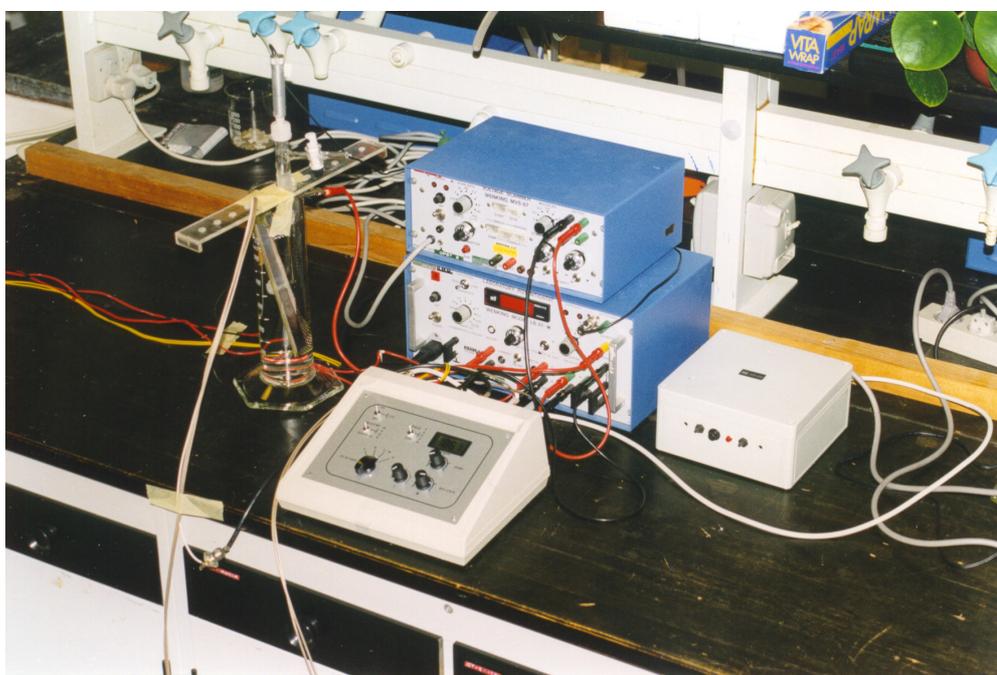


Figure 9. Photograph of experimental set up used in the potential scan experiment.

A continuous potential scan in the region -1000 to $+400$ mV (SCE) was applied using a scan rate of 30 mV/minute. Co-ordinate values of coupon potential, applied current, and differential resistance dR were recorded once every minute throughout the scan using a datalogger (CR-10X from Campbell scientific). Using a spreadsheet, dR/dt was calculated.

5. Results and discussion

The results from the measurements of coupon resistance as a function of temperature are presented graphically in figure 10. The theoretical data from figure 6 (and equation (9)) are included for comparison.

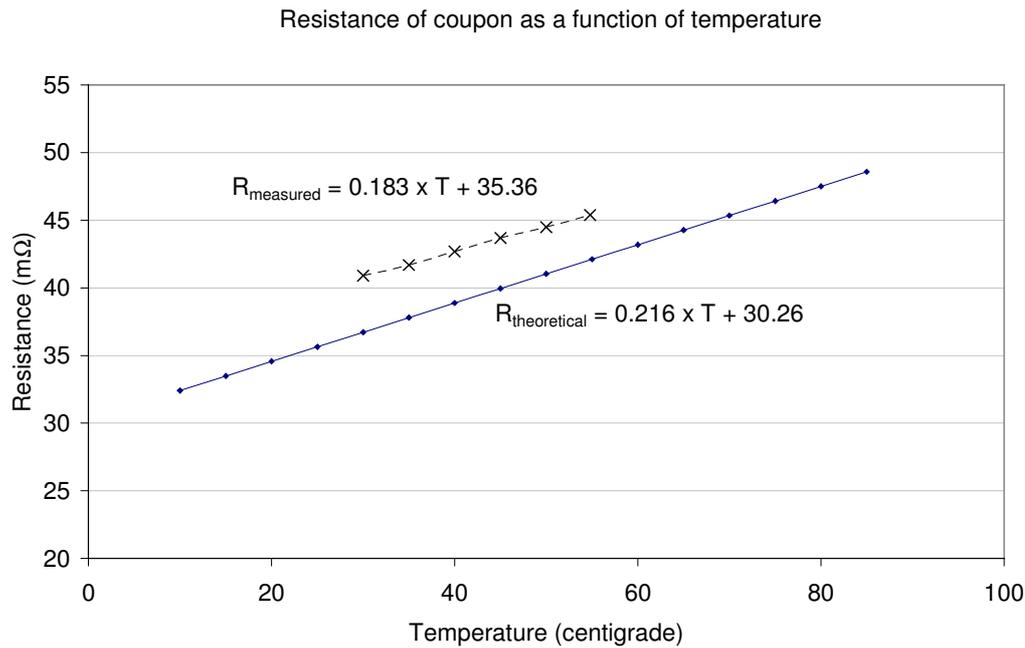


Figure 10. Graphical presentation of the measured coupon resistance as a function of temperature.

As observed from the figure, the measured coupon resistance is about 5 mΩ higher than the theoretical values. This is not surprising since the coupon was made from a steel foil with impurities. Further, the foil was received in a rolled condition. It is well documented that pure iron is more conductive than steel. The measured values can be expressed by the equation:

$$R_C(\text{m}\Omega) = 0.183T (\text{°C}) + 35.36 \quad (11)$$

As a consequence of the linear correlation between temperature and the foil resistance, the resistance of the reference can be used to measure the temperature of the environment in which the coupon is exposed (since the reference does not corrode during exposure).

Calculating the actual K value from equation (8), and inserting this and the resistance at 20°C into equation (7), the following correlation between corrosion rate and dR/dt is achieved for a temperature = 20°C:

$$V_{\text{corr}} (\text{mm/y}) = 0.23 \cdot \frac{dR}{dt} (\mu\Omega/\text{minute}) \quad (12)$$

The results from the DC-polarisation scan are presented in figure 11 in terms of the current density and dR/dt versus potential. As observed, the dR/dt measurement register very well the anodic dissolution of the steel coupon and performs excellent in detecting the immune, active, and passive region of the steel.

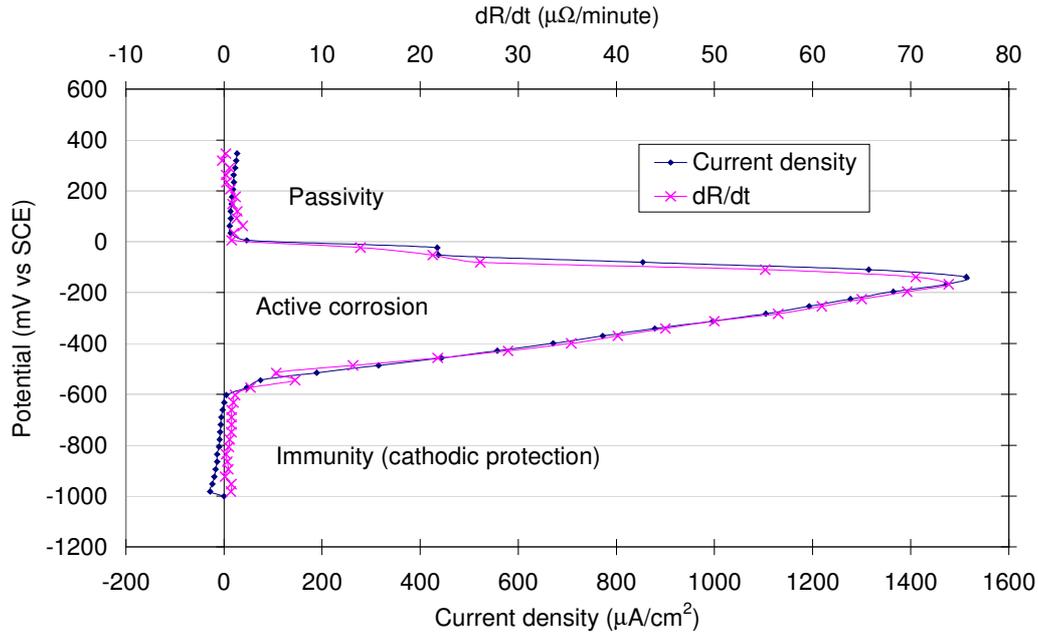


Figure 11. Results from the DC-polarisation scan in terms of the applied current density and dR/dt versus potential.

It is well established from corrosion theory that the anodic current can be converted into the corrosion rate according to the formula:

$$V_{\text{corr}} (\text{mm/year}) = 11.6 \times I (\text{mA/cm}^2) \quad (13)$$

where I is the applied anodic current density. The formula is established by simple dimension analysis, and in the present case, the formula can be applied at high anodic current densities that far exceed the open circuit corrosion current density. Accordingly, by calculating the corrosion rate using anodic current densities in the region 800-1500 $\mu\text{A/cm}^2$, a reliable comparison between the corrosion rate calculated from equation (13) and the corrosion rate calculated from equation (12) can be made. This comparison is presented in figure 12 showing an excellent correlation. A data fit gives the correlation:

$$V_{\text{corr}} (dR/dt) = 0.987 \times V_{\text{corr}} (\text{current density}) + 0.32 \quad (14)$$

This very fine correlation is taken as a strong evidence that the ER-technique presented in the present paper seems to be a powerful alternative to traditional techniques both when it comes to techniques applied for measuring accumulated corrosion and techniques applied for measurement of the instant corrosion rate. Naturally, a range of tests still needs to be performed, e.g. the performance of the technique at low corrosion rates (may be conducted by comparison with electrochemical impedance measurements in carefully selected environments where the impedance technique is well established), and the dR/dt response under local corrosion (pitting) conditions.

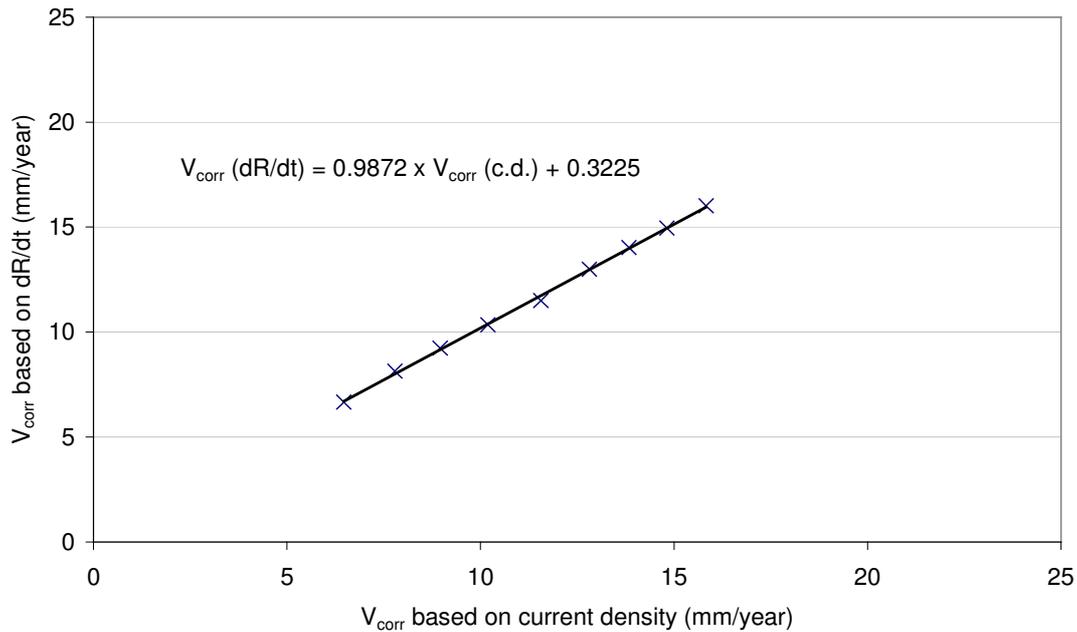


Figure 12. Comparison of corrosion rate based on applied anodic current density and corrosion rate based on dR/dt .

6. Conclusions

1. An ER probe with associated micro-ohmmeter has been designed, manufactured, and tested for its applicability in measurement of the general instant corrosion rate of steel. The concept is based on a differential measurement of the changes of the resistance (dR) due to corrosion of a thin steel foil (coupon) relative to a reference foil. The foil is mounted on a printed circuit board. The concept allows for measurement of the absolute resistance of the coupon and the reference as well, which can be used to monitor the degree of accumulated corrosion. The theoretical background for the measurements has been presented.
2. The theoretical considerations showed that the corrosion rate of a metal plate can be estimated by measuring co-ordinate values of dR/dt and R . The temperature has to be known as well. The challenge in designing an ER-concept suited for measurement of instant corrosion rate include that the measurement has to be very sensitive in order to measure the corrosion rate quick enough to avoid changes of the coupon resistance. Otherwise, the theoretical background for the measurement becomes invalid. Secondly, the ER-measurement is very sensitive to even very small temperature variations.
3. Firstly, the effect of the temperature on the coupon resistance was measured in the temperature range 30-55°C showing a fine linear dependency close to the theoretical behaviour. Accordingly, the temperature of the environment in which the measurement is made can be estimated by measuring the resistance of the

reference foil. Further, the temperature dependency was used to calculate a specific correlation between measured dR/dt and corrosion rate.

4. Secondly, the ER signal in terms of dR/dt was compared with the polarisation curve established by a continuous potential scan using a scan rate of 30 mV/minute in an acetic acid buffer solution at pH = 6. It was shown that the ER probe performed excellent in detecting changes in the state of corrosion (cathodic protection, enhanced anodic dissolution, and passivity). In addition, a comparison between the corrosion rate measured by the ER-technique and the corrosion rate calculated from the applied anodic current density showed a fine correlation:

$$V_{\text{corr}} (dR/dt) = 0.987 \times V_{\text{corr}} (\text{current density}) + 0.32$$

5. As a whole, the ER concept seems to be very promising and applicable in a range of corrosion studies in the laboratory as well as for monitoring purposes. In particular, the concept may be used in cases where the corrosion cannot be quantified by simple electrochemical means (atmospheric corrosion, corrosion of reinforcement in concrete, AC induced corrosion, corrosion under insulation, microbial corrosion in sulphide environments, etc.).

7. References

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