DETERMINATION OF CARBON STEEL CORROSION RATE AT LOW CORROSION POTENTIALS BY MEANS OF A NEW ELECTROCHEMICAL METHOD

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Abstract

Determination of corrosion rate by means of electrochemical methods such as polarization resistance is limited to open-circuit conditions. In the case of cathodic protection, a protected object is polarized to protection potential by means of negative total current, the value of which is thus useless for quantifying corrosion rate. Long-time response physical methods, such as weight loss or electrical resistance technique are only applicable for corrosion rate determination under cathodic polarisation. A novel electrochemical method employing two working electrodes allows us to determine instantaneous corrosion rate at impressed potential even if the total current is negative. Anodic current density is extracted from two consecutively measured currents. The shape of the carbon steel corrosion rate curve at the impressed potential in the potassium carbonate solution was determined. At pH 11, carbon steel was spontaneously passive, however, at cathodic polarization to the Kuhn's protective potential, substantially elevated corrosion rate was indicated. The shape of the corrosion rate - impressed potential curve was confirmed by electrical resistance sensors exposed to aerated aqueous electrolyte under the same conditions.

Keywords: Double-electrode, cathodic protection, corrosion rate, carbon steel

1. INTRODUCTION

The general statement about the rate of oxidation reactions, such as corrosion, is that it decelerates with the declining electrode potential, nevertheless only if the rate depends on the charge transfer rate at the metal - electrolyte interface. This assumption is how the principle of cathodic protection and the establishment of an empiric criterion -850 mV/CSE (Kuhn‘s protective potential) [1], [2] used for cathodic protection of buried steel structures are explained. What is substantially less mentioned is the fact that at cathodic protection in environments where the transport of electrochemical reactions products from the polarised steel surface is limited, the pH of electrolyte substantially grows [3]. High pH levels (exceeding 13) of soil electrolyte were observed which indicates that the passivation potential of carbon steel under those pH levels could have been expected to be more negative than the protection potential [4], [5]. In such a case, the protective function of cathodic protection is not essentially based on suppression of the corrosion rate in active state but on the active-to-passive transition of carbon steel as a result of altered composition of the environment at the polarised surface [6], [7]. Not only pH increase, but also the drop of concentration of negatively charged corrosion stimulators (Cl^-) upon the cathodically polarised surface by migration in the electric field plays an important role in the steel transition into the passive state [8].

In principle, for each metal that is in passive state under given conditions, there is a zone of activity at the potential that is more negative than the passivation potential. Thus, it may happen that the metal is cathodically protected with the protective potential being more negative than -850 mV/CSE and the total protective current is negative (the cathodic reaction on the protected object prevails over the anodic reaction), however, compared to the situation with a more positive protective potential, the corrosion rate would be unacceptable (EN 12954, 20014; ISO 15589-1, 2003) [15]. It is obvious that if such situation happens, measurement of the protective potential and protective current as a cathodic protection intensity rate will be insufficient. Corrosion rate of a cathodically protected metal should be directly monitored.

Corrosion rate of metals is most frequently measured by long term exposure of corrosion coupons [2], [6], [9], [10]. The electrical resistance technique almost continuously indicates corrosion loss by increase of electrical resistance of a thin layer of the exposed metal [9], [11], [12], [13], [14], [15], [16], [17] and it is recommendable for corrosion monitoring. Electrochemical methods, e.g. polarisation resistance, are not applicable at impressed potential, as in the case of cathodic protection.

This study deals with an electrochemical technique for determining the corrosion rate of a cathodically protected metal by an extraction of current corresponding to the rate of the anodic reaction out of the total protection current.

2. EXPERIMENTAL PART

The carbon steel corrosion rate vs. impressed potential curve was determined by means of the newly designed double-electrode, which enables extraction of the current corresponding to the rate of carbon steel anodic reaction from the current impressed by the potentiostat. The double-electrode consists of two working electrodes that are not conductively interconnected. One of the working electrodes used in this study was made of 1.0115 grade carbon steel and the other one of 1.4404 stainless steel (the steel numbers follow the EN 10027-2 standard) with the approximate composition of FeCr17Ni12Mo2 and the carbon content being lower than 0.03 wt. %. In principal, one of the working electrodes should be made of a metal, the corrosion rate of which is to be determined and the other working electrode should be resistant to corrosion in a given environment so that its oxidation rate is negligible. The shape of both working electrodes was cylindrical with 19 mm in diameter and 14 mm high with the cylinder shell to be exposed. The exposed surface of each working electrode was 8.4 cm^2. The stainless steel working electrode was ground with SiC emery paper (P320) and then passivated in a 30% solution of HNO_3 (60 °C, 30 minutes). The stainless steel working electrode was then only washed with demineralised water and with ethanol between the tests. The carbon steel working electrode was ground by SiC emery paper (P320) before each measurement. After grinding the specimen was rinsed with ethanol. The double-electrode scheme is pictured in **Figure 1**. An important parameter is that exposed surfaces of both working electrodes (a) and (b) are identical and that they are not galvanically interconnected. However, the working electrodes are mutually short-circuited by a copper conductor (c) during the first phase of the measurement. The exposed surface is limited by heat-shrinkable tube (d) and a PTFE part, which covers the pin closure (**Figure 1**).

The double-electrode is a part of a corrosion cell that consists of a lockable jar with a reference electrode (saturated calomel electrode - SCE) and an auxiliary platinum wire electrode inserted through the cover. The jar is equipped with an inlet for inert-gas injection into the electrolyte and with an outlet equipped with a water seal for the inert gas passed through the electrolyte. The volume of the jar is 1000 ml, which ensures negligibility of any deviations in the electrolyte composition induced by cathodic polarisation. The electrochemical corrosion system PC3 by Gamry Instruments, Inc. served as the potential-controlled source of power.

The measurement with a double-electrode consists of two phases. In the first phase, the working electrodes are short-circuited by an external conductor (c). The treated double-electrode is inserted in electrolyte and connected to the source of current set on the selected level of potential. The current vs. time curve is scanned for a given period of time. After that the external conducting connection is interrupted and only one of the working electrodes remains polarised. For the sake of this study, it was decided that both phases would last 20 minutes.

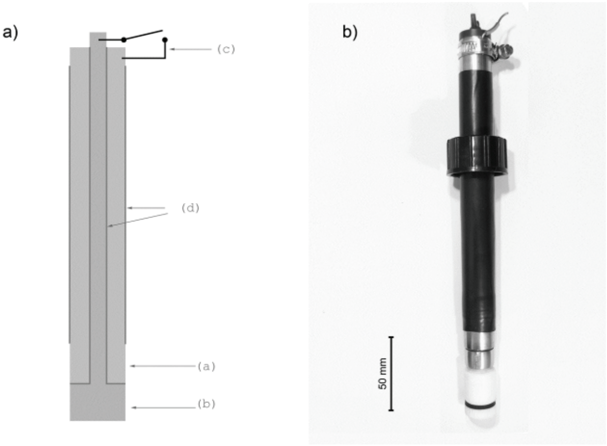

Figure 1 A scheme a) and a photograph b) of the double-electrode ((a) - stainless steel working electrode, (b) - carbon steel working electrode, (c) - electrical switch, (d) - insulation)

The partial anodic reaction rate (corrosion rate) at a given impressed potential is derived from two consecutively measured total currents that correspond to the sum of anodic and cathodic currents of stainless steel (a) and carbon steel (b). When the stainless steel working electrode (a) and the carbon steel working electrode (b) are galvanically interconnected, the total current supplied by the direct-current source (a potentiostat) equals to the sum of both cathodic currents and both anodic currents (1), of which the anodic current on stainless steel (a) is negligible (polarisation resistance values measured in triplicate after 20 minutes were 0.9, 1.2 and 3.3 Ω·m^2 in the case of carbon steel and 34.8, 46.2 and 51.2 Ω·m^2 in the case of stainless steel).

$$I_{T1} = I_A + 2I_C \qquad (1)$$

$$I_{T2} = I_A + I_C \qquad (2)$$

Where current (I) subscripts mean A - anodic, C - cathodic and T - total. After electron-conductive disconnection of the stainless steel working electrode (a), when only the carbon steel working electrode (b) is polarised, the total current equals to the sum of only anodic and cathodic reactions on carbon steel (e), i.e. (2).

Results of these two equations give us the value of partial anodic current, out of which it is possible to calculate the corrosion rate at a given potential. The calculation is valid if the inert electron-conductive material (a) shows a negligible corrosion rate ($I_{A1} = 0$) and the rate of cathodic reactions on both materials (a) and (b) is identical ($I_{C1} = I_{C2}$). Undoubtedly, that applies in the potential interval, within which the oxygen reduction rate is controlled by the rate of diffusion towards the surface, i.e. under limiting current control.

The double-electrode was tested in an electrolyte with pH of 11 that was prepared from $KHCO_3$ solution (p.a.) in demineralised water. pH of the electrolyte was adjusted by KOH (p.a.) solution to the required level. All measurements proceeded at an ambient temperature. The electrolyte was purged with 99.9% purity technical nitrogen 30 minutes before and during the test.

3. RESULTS AND DISSCUSION

The carbon steel corrosion rate vs. impressed potential curve was obtained by the potentiostatic polarisation the double-electrode (**Figure 2**). Potentiostatic polarisation of the double-electrode proceeded 40 minute in total. The curve connecting the points takes an anticipated shape of a partial anodic polarisation curve corresponding to the active-to-passive corrosion state transition.

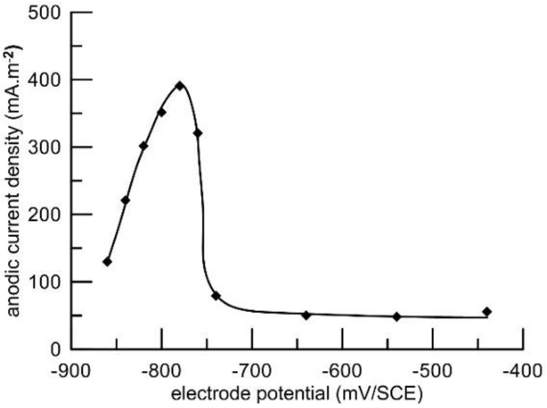

Figure 2 The iron anodic reaction rate vs. corrosion potential curve at pH 11 measured by the double-electrode

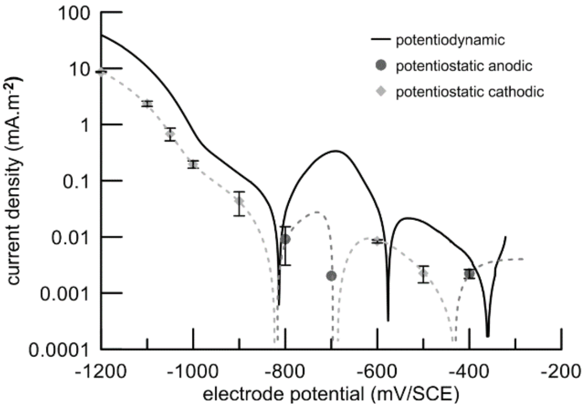

Figure 3 Potentiodynamic (1 mV·s^{-1}) and potentiostatic (40 minutes) polarisation curves for carbon steel single electrode in deaerated pH 11 carbonate solution

The results obtained describe conditions for the carbon steel active-to-passive state transition in the environment of potassium hydrogen carbonate. The recorded points clearly follow the typical trend of metal's active-to-passive state transition. Corrosion rates plotted for the double-electrode in **Figure 2** were obtained using the above-mentioned calculation from total currents measured after 20 minutes of exposure.

The advantage of determination of a metal's (in this case carbon steel's) corrosion rate by means of the double-electrode is its low requirements for the deaeration of the testing electrolyte. If we wanted to determine corrosion rate of a cathodically polarised metal from the passing current, we would have two options depending the corrosion behaviour of the respective metal. Should the corrosion rate of the metal was low and the anodic reaction rate (corrosion of the metal) was notably lower than the rate of the environment component (e.g. oxygen, water) reduction, it would be possible to consider the total negative (cathodic) current as an intensity of the cathodic reaction and thus as well as an estimate of the rate with which the metal would corrode, unless protected. However, it would only be feasible in the potential region, in which the oxygen reduction rate is controlled by the transport.

The other case is a situation, when the transition to an active state would be initiated at cathodic polarisation of the passive metal. At a given potential, the anodic process would prevail over the cathodic reaction and the total current would be positive. This positive current could be again used for estimation of the corrosion rate at a given potential, however, only if the anodic current were significantly higher than the current corresponding to the cathodic reaction so that the intensity of the cathodic process would not impact the total current notably. This would mean though that oxygen would have to be perfectly eliminated from the electrolyte and that measurements would have to be performed in regions, where water-to-hydrogen reduction does not take place or is negligible.

Such an approach leads to identification of potential regions, where steel corrosion rate grows as a result of cathodic polarisation (**Figure 3**). Approximately within the range of -700 to -850 mV / SCE the total current was positive at potentiostatic polarisation in a partly deaerated electrolyte. This region was assessed as an area of elevated steel corrosion rate due to cathodic polarisation and it approximately matches the region of activity identified by means of the double-electrode.

Figure 3 is separable into two parts with negative total current and two parts with positive current is in good agreement with the shape of the cathodic polarisation curve measured in the partly deaerated electrolyte (0.5 mol·l^{-1} $KHCO_3$ + KOH; pH 11), which three times in total crosses the potential axis (Type II of the sum curve - passivable metal, limited control of the environment element reduction [18]).

The impact of deaeration, though not explicitly determined, is apparent from two different curves of I vs. t measured at potentiostatic polarisation of the double-electrode (**Figure 4**). One of the curves corresponds to the insufficiently deaerated environment, in which oxygen reduction still strongly applies at the given potential. The original free corrosion potential (E_{corr}) of -360 mV / SCE indicated the presence of an aerobic environment. As to the other curve (E_{corr} = -836 mV / SCE), no significant change of the total current was identified after de-connection of the working electrode from stainless steel.

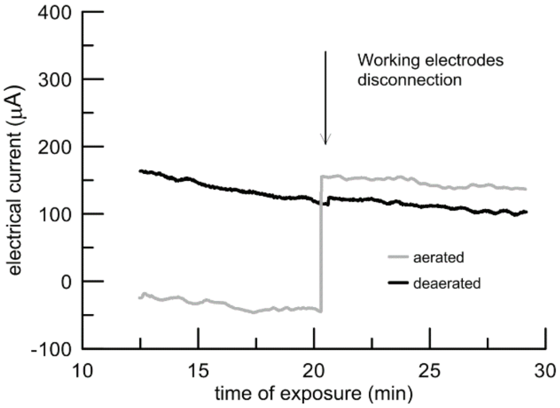

Figure 4 Potentiostatic polarisation record of the double-electrode at -550 mV / SCE in pH 11 carbonate solution when aerated or deaerated

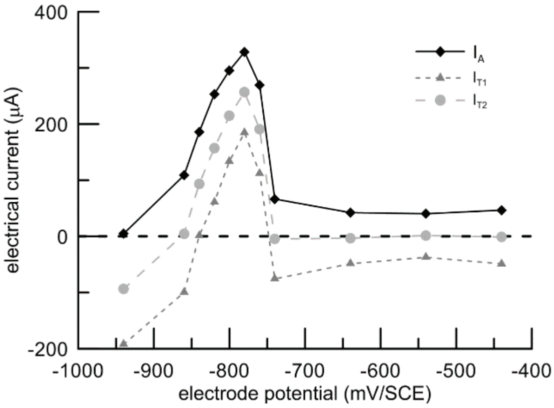

Figure 5 Electrical current output from the double-electrode potentiostatic measurement (I_{T1} - total current when both the working electrodes are polarised, I_{T2} - total current when only carbon steel working electrode is polarised, I_A - anodic current of carbon steel working electrode as calculated from I_{T1} and I_{T2})

The double-electrode benefits are depicted in **Figure 5**, where current values obtained at the potentiostatic polarisation are plotted. One set of the tests (I_{T1}) contains levels of the total current, i.e. the current corresponding to the sum of the anodic current on carbon steel (I_A), cathodic current on carbon steel (I_{C2}) and cathodic current on stainless steel (I_{C1}). The curve connecting the points has a traditional shape of a polarisation curve of passivated metal [19]. The other set of values representing the total current I_{T2} (the sum of I_A and I_{C2} at the carbon steel working electrode) has an identical shape as the I_{T1} curve with the values being shifted in a positive direction by the value of I_{C1} current, which does not apply here. Eventually, the I_A curve represents current levels corresponding purely to the rate of the anodic reaction on carbon steel. It is obvious that at various levels of the solution deaeration the points follow the anticipated curve I vs. t for a partial anodic reaction including the active-to-passive transition.

4. CONCLUSION

Corrosion rate of a cathodically polarised metal is difficult to be measured by electrochemical techniques. Corrosion rate can be estimated from the protective current, but only if the anodic process prevails over the cathodic one even during cathodic polarisation. This may happen, for instance, if a metal in a passive state is polarised to the potential level that is more negative than the passivation potential. Such behaviour was reported for steel in an alkaline carbonate solution. However, the overall protective current is lower than the current corresponding to the corrosion rate. A combined working electrode composing of specimens of carbon and stainless steels can be used to separately calculate corrosion rate of carbon steel, even if it is cathodically polarised and the overall protective current is negative. It all applies on the condition that the cathodic reaction rate on both parts of the working electrode is identical at a given potential and that the corrosion rate of the stainless steel specimen is negligible in the given environment compared to the corrosion rate of the carbon steel specimen.

ACKNOWLEDGEMENTS

Financial support of the Czech Science Foundation (project 14-20856S) is gratefully acknowledged.

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