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Limitations of the linear polarization method to determine stainless steel corrosion rate in concrete environment

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Abstract

The linear polarization is a non-destructive way of estimating the instantaneous corrosion rate of a metal. In case of reinforced concrete, the method is restricted mainly because of a concrete resistance, unknown area of the polarized reinforcement and non-uniform corrosion. In spite of that, thanks to the polarization resistance it is possible to estimate whether the reinforcement corrodes in activity or passivity. The results imply that sometimes even the knowledge of R_p is insufficient for stating activity or passivity of the material. It has been proved, however, that the shape of the curve determining R_p by linear polarization may frequently indicate the corrosion behaviour. It is possible to evaluate the deviation of the point of zero current from the free corrosion potential which was measured prior to the linear polarization and also to evaluate the deviation of the polarization curve from the regression line, which is defined by the coefficient of determination.

Keywords: Polarization resistance; Linear polarization; Concrete reinforcement; Stainless steel

1. Introduction

Linear polarization is a non-destructive method designed for measuring polarization resistance. Therefore, it serves for identification of corrosion rate at or near free corrosion potential. The potentiodynamic way of linear polarization technique is based on a continuous change of an electrode's potential in the vicinity of free corrosion potential. Prior to each measurement, free corrosion potential must be identified with a reference electrode. Subsequently, a counter electrode makes the working electrode's potential skip in the cathodic direction. Polarization of the working electrode in anodic direction follows with a constant scan rate up above the value of corrosion potential. The working electrode gets thus slightly excited, symmetrically in the vicinity of the corrosion potential within the potential range $\Delta E = E - E_{corr}$ in both anodic and cathodic direction.

The standard ASTM G 59–91 (Standard test method for conducting potentiodynamic polarization resistance measurements) [1] defines the polarization resistance by the relation Eq. (1).

$$R_p = \left(\frac{\partial \Delta E}{\partial i}\right)_{i=0, \mathrm{d}E/\mathrm{d}t \to 0} \tag{1}$$

It means that the polarization resistance of a corroding electrode is defined as a slope of a potential-versus-current density line within the zero current point $i = 0$. The rate of polarization should be close to zero.

The polarization resistance value is then used for calculating the corrosion rate in a form of the corrosion current density (i_{corr}) by using Eq. (2).

$$i_{corr} = \frac{B}{R_p} \tag{2}$$

However, for the coefficient B, Stern–Geary coefficient, the Tafel slopes b_a, b_c must be known (Eq. 3). Mostly, the coefficient is strictly empirical for a given corrosion system.

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Nomenclature

List of symbols

E	electrode potential
R_p	polarization resistance
E_{corr}	free corrosion potential
i	current density
I	current
R_e	electrolyte resistance
t	time
i_{corr}	corrosion current density
B	Stern–Geary coefficient
b_a, b_c	Tafel slopes
E_{oc}	open-circuit potential prior to linear polarization
$E_{i=0}$	zero current potential (potential of the intersection of polarization curve and zero current coordinate)
R^2	coefficient of determination of linear regression

$$B = \frac{b_a b_c}{2.303(b_a + b_c)} \tag{3}$$

Fortunately, it is not essential to know the Tafel slopes in case of steel reinforcement in concrete because the knowledge of the limit value of polarization resistance itself is sufficient for distinguishing between corrosion in activity or in passivity. The following conversion of polarization resistance into corrosion rate is merely an implication of a new error into results. Moreover, corrosion attack is of a localized character in case of concrete reinforcement, thus it is impossible to identify corrosion rate within the attack with the calculated corrosion rate representing a mean value of corrosion rate in a polarized area of an electrode.

In case of steel in chloride-free concrete pore solution, it can be expected that linearity of linear polarization curves will be affected by difference in values of anodic and cathodic Tafel slopes which correspond to diffusion control and charge-transfer control, respectively. In this case, a plot of E versus i will tend to curve to an asymptote parallel to the potential axis. The difference between the values b_a and b_c not only modifies the equation for calculating the coefficient B but it affects the technique of polarization resistance determination. The higher the difference between the values b_a and b_c, the narrower the range that would be utilizable for the analysis [3]. The problems of polarization curves' non-linearity in the vicinity of corrosion potential were thoroughly dealt with by Mansfeld [4]. Mansfeld proved that linear curves can be expected only in exceptional cases ($b_a = b_c$) and that determination of polarization resistance through linearization procedure can lead to erroneous values [4]. No curve, however, can ever be said to be linear. For cases where b_a approaches infinity (stainless steel in oxygen saturated acids) or b_c approaches infinity (corrosion under diffusion control), the deviation from linearity would be even larger [6]. Many errors in polarization resistance results, which were obtained by means of commercial corrosion monitoring probes, originate in the assumption that the polarization curve is linear up to the specified overvoltage, usually 10 mV [7]. These devices determine the current at a given potential and calculate the slope between this point on the polarization curve and the origin ($E - E_{corr}$).

It is expected for correct measuring by means of linear polarization that free corrosion potential is stationary prior to polarization [3]. During the measurement, the system being polarized with a given rate of polarization requires some time to achieve a steady-state [2]. High rate of polarization contributes to non-stationarity of the system by a double layer capacitance charging effect [1]. In case of potentiodynamic polarization, the requirement of the steady-state could be achieved by a low rate of polarization. For very fast polarization, when t approaches 0, the equation of a current response can be simplified to [2]:

$$\frac{dI}{dE} = \frac{1}{R_e} \tag{4}$$

and for very low polarization rate [2]

$$\frac{dI}{dE} = \frac{1}{R_e + R_p} \tag{5}$$

Assuming these two equations and low electrolyte resistance, it can be expected, when performing the potentiodynamic measurement within short potential range in the vicinity of free corrosion potential, that the polarization curve will be of a very sharp slope ($1/R_e$) at the beginning of polarization and $1/(R_e + R_p)$ after a long period of time, resulting in a non-linear polarization curve.

This study discusses the results of determination of polarization resistance by means of linear polarization which were primarily collected to estimate the threshold chloride level for activating several types of stainless steel in fresh as well as in carbonated concrete pore solutions. Some unexpected values of R_p led to a detailed survey of the originally measured data. The paper presents results of the non-linear polarization curves analysis.

2. Experimental

Since the linear polarization method was primarily used for assessing the threshold chloride level at which several types of stainless steel became locally activated, five stainless steel grades were selected and exposed to concrete pore solutions differing in pH (8, 12.5, 13.5) and chloride content (from 0.1 up to 150 g of chloride ions/l). It is not essential to specify the composition of stainless steels within the scope of this paper, it is sufficient to present the approximative composition and prevailing structural phase (FeCr12—martensite, FeCr16—ferrite, FeCr18-Ni10—austenite, FeCr18Ni10Mo2—austenite, FeCr22-Ni6Mo3—austenite–ferrite). The stainless steels were used in form of flat specimens which were cut from a steel pole or prism. The specimens were fixed to the corrosion cell equipped with an integrated counter and reference electrode. The specimen served as the cell's bottom. The exposed area (2.54 cm^2), defined by a gasket, was overlayed with 30 mm thick layer of the electrolyte. Since the surface of the stainless steel reinforcement may be contaminated with scales the origin of which could be in manufacturing process or welding, the effect of scales on corrosion resistance of the stainless steel specimen has been investigated. In that case, the specimens were heat treated at 1080 °C for 15 min. Most of the linear polarization measurements were performed after free corrosion potential stabilization, which occurred usually after three days of exposure, within the potential interval -10 up to $+10$ mV with respect to free corrosion potential. Free corrosion potential was measured as an open-circuit (E_{oc}) for 10 s right before the linear polarization. Immediately after that the specimen was polarized to -10 mV with respect to that free corrosion potential (E_{oc}). Potential of the specimen was then continuously increased up to $+10$ mV versus E_{corr}. Current density was recorded simultaneously. Originally, the rate of polarization was adjusted to 0.5 mV/s but later on, different values of scan rate (1, 0.125, 0.04 mV/s) were tested.

3. Results and discussion

The resulting threshold chloride levels for stainless steel activation in carbonated and fresh concrete pore solution are presented elsewhere [5]. At this point, the only results presented herein are those complicated for analysis due to nonlinear course of linear polarization curves.

The linear polarization curve measured at martensitic stainless steel FeCr12 is presented in Fig. 1. The potentiodynamic measurement proceeded as described in the experimental part above. The scan rate in this case was adjusted at 0.5 mV/s. The curve corresponds to forward scan, i.e. from the cathodic region toward the anodic region. It is apparent that the curve section situated negatively, in terms of potential, with respect to the open-circuit potential E_{oc} (the free electrode potential prior to linear polarization; corresponding to the free corrosion potential at stationary conditions) is considerably non-linear, which confuses the determination of the polarization resistance value to a certain extent. As the definition of polarization resistance says (Eq. (1)), polarization resistance is a slope of a tangent adjacent to a linear polarization curve, measured by using infinitely low scan rate under stationary conditions, at the point of zero current density. If we apply the zero current rule, the slope of the tangent gives polarization resistance 73 Ω m^2. As we can see in the Fig. 1, the zero current point does not correspond to the steady state potential of the specimen (E_{oc}). The zero current potential, which can be specified as a new corrosion potential, shifted by 4.5 mV cathodically from the E_{oc}. However, that corrosion potential does not correspond to stationary conditions due to nearly negligible cathodic polarization. Nevertheless, the demand of stationary conditions cannot be fulfilled at any case because the scan rate has to always be of a finite value. Cathodic polarization, even by 10 mV with respect to E_{oc}, moves the corrosion potential of an easily polarizable electrode (in a passive state) in a cathodic direction and it obviously takes some time to reach the steady-state again. If we omit the fact that E_{oc} does not correspond to the zero current point, the analysis in the vicinity of the E_{oc} gives significantly higher R_{p} which is equal to 137 Ω m^2, however, even this way of analysing does not follow the definition of the polarization resistance (Eq. (1)). On the other hand the analysis carried out at the zero point current may lead to underestimation of the polarization resistance.

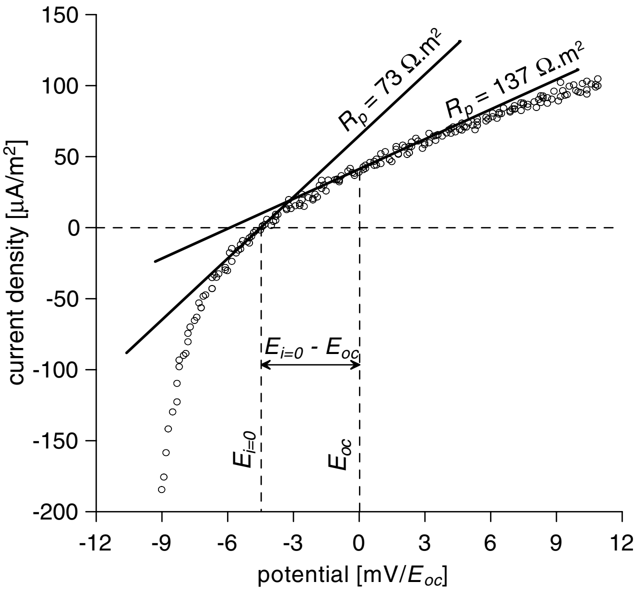
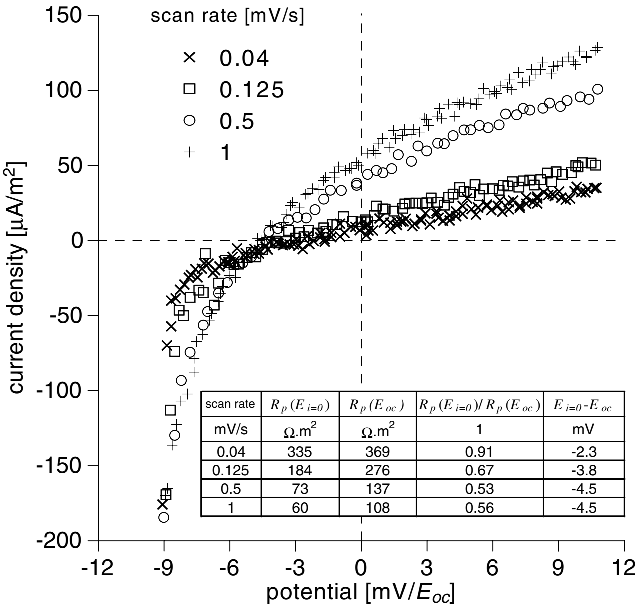


Fig. 1. Polarization curve obtained by potentiodynamic polarization (-10 up to $+10$ mV/E_{oc}, 0.5 mV/s) for FeCr12 (bare surface) after three days of exposure in fresh concrete pore solution (pH 12.5) contaminated with chlorides (15 g Cl$^-$/l).

It is obvious that the reduction of scan rate may help the electrochemical system to approach the steady-state [2], but the linear polarization curves remain non-linear even at very low scan rates, as might be seen in Fig. 2. As the scan rate becomes lower, the shift of zero current potential from the E_{oc} decreases. Consequently, the zero current point moves slightly forward to the less non-linear section of the polarization curve and the polarization resistances determined in the vicinity of E_{oc} and zero current potential respectively, are less divergent in their values, which can be characterized by ratio of the two values, and the difference between the two ways of analysis mitigates.



scan rate	$R_p(E_{i=0})$	$R_p(E_{oc})$	$R_p(E_{i=0})/R_p(E_{oc})$	$E_{i=0}-E_{oc}$
mV/s	Ω.m²	Ω.m²	1	mV
0.04	335	369	0.91	-2.3
0.125	184	276	0.67	-3.8
0.5	73	137	0.53	-4.5
1	60	108	0.56	-4.5

Fig. 2. Polarization curves obtained by potentiodynamic polarization (-10 up to $+10\,\mathrm{mV}/E_{oc}$) at various scan rates for FeCr12 (bare surface) after three days of exposure in fresh concrete pore solution (pH 12.5) contaminated with chlorides (15 g Cl^-/l).

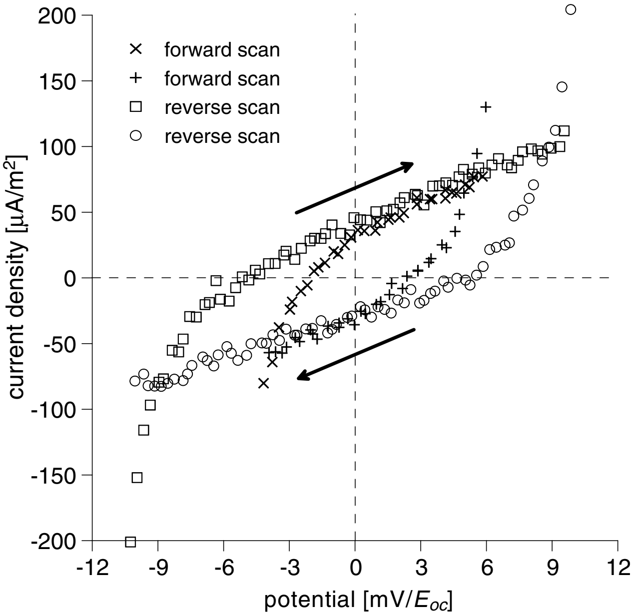


Fig. 3. Polarization curves obtained by potentiodynamic polarization (0.5 mV/s) within two different potential ranges ($\pm 5\,\mathrm{mV}/E_{oc}$; $\pm 10\,\mathrm{mV}/E_{oc}$) for FeCr12 (bare surface) after three days of exposure in fresh concrete pore solution (pH 12.5) contaminated with chlorides (15 g Cl^-/l).

Since the electrochemical system comprises the charge-transfer controlled oxygen reduction on the cathodic side and the diffusion controlled corrosion of passivated stainless steel on the anodic side, we may expect considerably dissimilar values of Tafel slopes. As mentioned in the introduction, this divergence may be responsible for the non-linearity of the polarization curves [4,6,7]. Should the non-linearity of the curve be given only by the divergence of Tafel slopes, the curve scanned in the opposite direction (from +10 mV up to $-10\,\mathrm{mV}/E_{oc}$) should display an identical course as the forward scan. Fig. 3 shows, in addition to the forward-scan polarization curve, the reverse-scan polarization curve that was measured at the identical specimen of FeCr12 after the spontaneous recover of free corrosion potential. The specimen was then polarized from +10 mV versus E_{oc} down to -10 mV versus E_{oc} with scan rate 0.5 mV/s. Since the same non-linearity as in case of forward scan was observed at the start of the curve, the non-linearity in such a small potential range is probably not caused by the divergence in Tafel slopes. The Tafel slope effect would probably occur when polarizing in a larger potential range. The other two curves emerging in the Fig. 3 prove this statement by their non-linearity which occurs even after the reduction of the potential range.

The increase of cathodic or anodic current density at the beginning of the polarization curves is induced by a sudden skip in potential at the starting point of the linear polarization measurement where the rate of polarization approaches infinity. At that point, as mentioned in the introduction, the slope of the polarization curve is approximately equal to $1/R_e$. The slope of the curve changes in time while approaching the value of $1/R_e + R_p$. Thus, determination of the polarization resistance in the point of $i = 0$, which follows the definition of polarization resistance [1], will lead to erroneous result due to non-linearity of a polarization curve. The extent of the non-linearity is given by the capacitance of the electrode double layer [2]. When polarized, the system needs some time to reach the steady-state again. The discharging effect can be clearly seen in the graphs of current density versus time under potentiostatic polarization at 5 and 10 mV versus E_{oc} in both anodic and cathodic directions (Fig. 4). The values of current density after their stabilization in time can be used for calculating polarization resistance. Considering direct current corrosion methods, these values should be the most revelevant under the assumption of the negligible effect of ohmic resistance of an electrolyte and linearity of the $i(E)$ function at the given potential range, the change of the electrochemical system caused by potentiostatic polarization, and the effect of non-Faradayic events are negligible, because the stabilized current density can be associated with an infinitely low scan rate which should be used when measuring by the linear polarization method. The values of polarization resistance resulting from the potentiostatic polarization are in the order of hundreds of $\Omega\,\mathrm{m}^2$, it means, considering the potentiodynamic polarization, that, as expected, only very low scan rates are able to provide appropriate results. However, even at 0.04 mV/s there are still several cases when the tangent passing through the zero current potential at the potentiodynamic polarization curve provides underestimated resistance values in the order of tens.

Recently, more that seven hundred individual linear polarization measurements were carried out at five grades

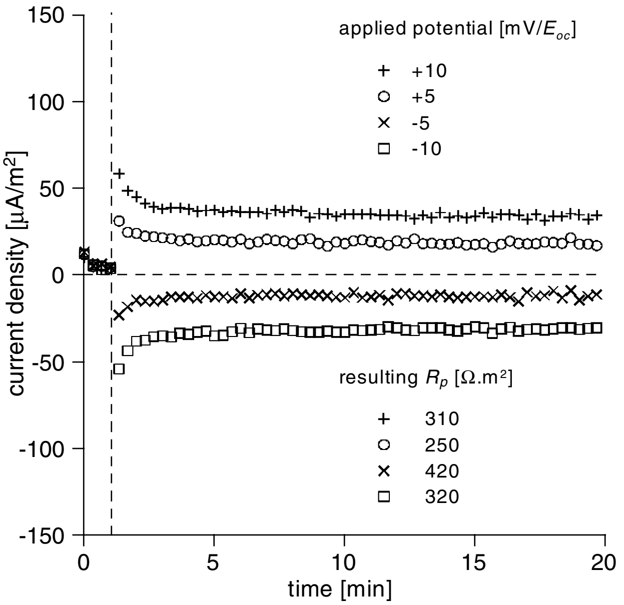


Fig. 4. Potentiostatic curves for FeCr12 (bare surface) after three days of exposure in fresh concrete pore solution (pH 12.5) contaminated with chlorides (15 g Cl^-/l). The potentiostatic polarization (−10, −5, +5, +10 mV/E_{oc}) was applied 60 s after the start of the curve scanning.

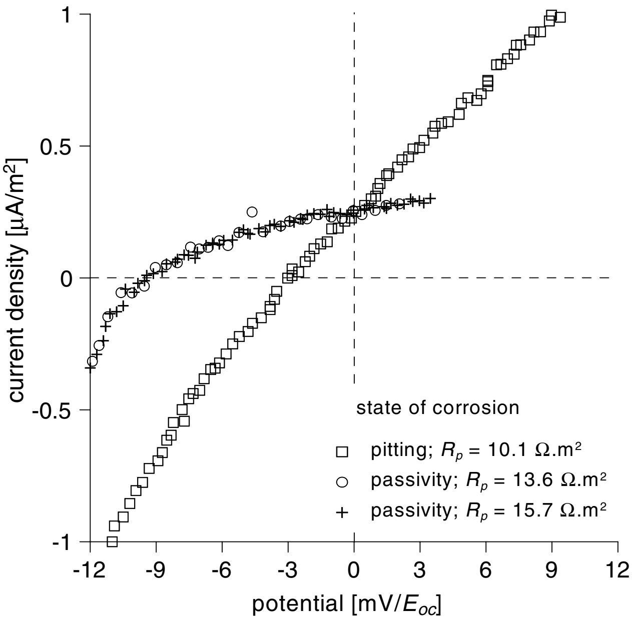


Fig. 5. Polarization curves obtained by potentiodynamic polarization (−10 up to +10 mV/E_{oc}, 0.5 mV/s) for FeCr16 (bare surface) after three days of exposure in carbonated concrete pore solution (pH 8) contaminated with chlorides (150 g Cl^-/l).

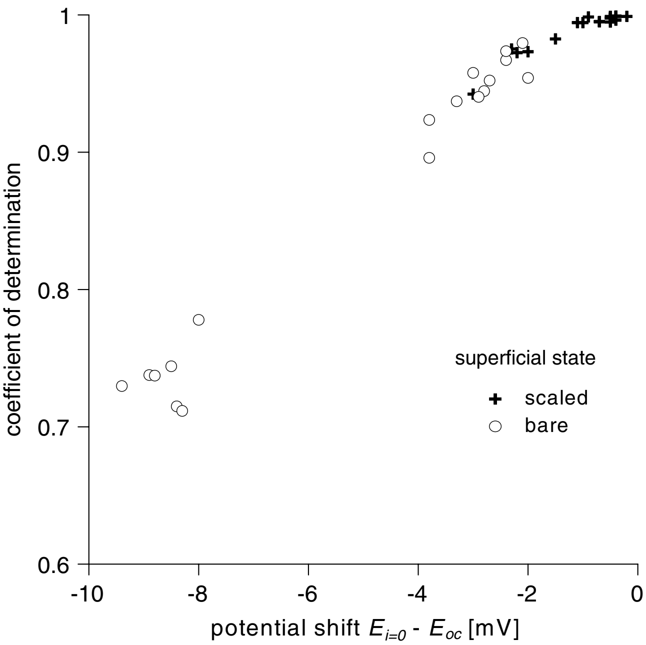


Fig. 6. Non-linearity of polarization curves expressed by coefficient of determination of linear regression and its relation to polarizability expressed by potential shift of zero current point potential with respect to open-circuit potential (FeCr12, −10 up to +10 mV/E_{oc}, 0.5 mV/s, pH 8, various chloride content).

of stainless steel exposed to fresh and carbonated concrete pore solution variously contaminated with chlorides. The stainless steels differed in their composition, phase structure and superficial state (bare, scaled). Usually, the specimens the polarization resistance of which was higher than 30 Ω m^2 were definitely passivated, on the other hand, polarization resistance in the order of units indicated corrosion in the active state. However, there were several cases in which linear polarization did not allow distinguishing between corrosion in activity and in passivity. For instance, linear polarization curves measured at a ferritic stainless steel which was exposed to carbonated concrete pore solution (pH 8) containing 150 g of chloride ions/l are presented in Fig. 5. Scanning of the polarization curves was performed at the rate of 0.5 mV/s and the polarization resistance values were determined in the vicinity of the zero current point. It is evident that such way of determination of polarization resistance leads to a considerable underestimation of the values since the non-linear curves, belonging to the specimens in passive state, give R_p values similar to those of the specimen in the active state.

To distinguish active and passive state in these cases, we used a very simple method which is based on linear regression of the data obtained. The coefficient of determination (R^2) enables the deviation of the linear polarization curve to be quantified on the basis of the ideal linear shape. The coefficient of determination was plotted against the potential difference between the zero current potential and the open-circuit potential. This difference ($E_{i=0} - E_{oc}$) characterizes an electrode's ability to be polarized. As can be seen in Fig. 6, the points are separated into two different groups. The first group defined by low value of $E_{i=0} - E_{oc}$ and R^2 approaching 1 corresponds to the specimens activated by chloride ions. In case of martensitic stainless steel with scaled surface, all the specimens got activated in carbonated concrete pore solution even at a very low chloride concentration (0.1 g/l). Having cleared FeCr12 steel off of

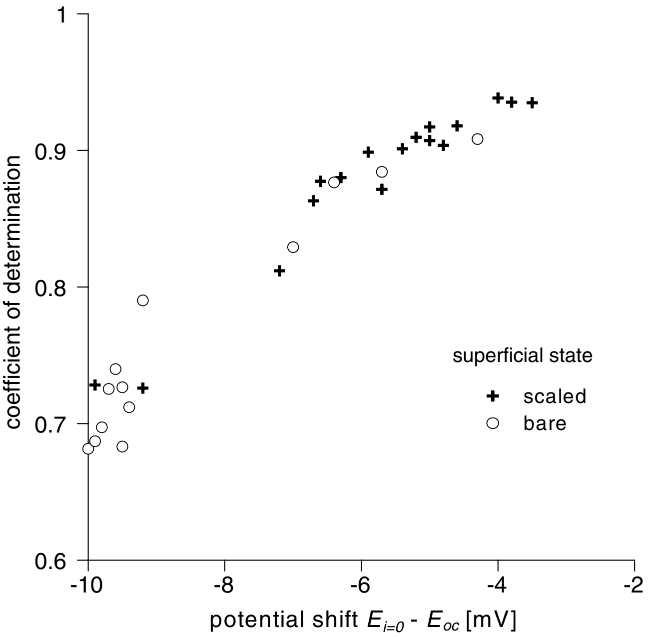


Fig. 7. Non-linearity of polarization curves expressed by coefficient of determination of linear regression and its relation to polarizability expressed by potential shift of zero current point potential with respect to open-circuit potential (FeCr12, −10 up to +10 mV/E_{oc}, 0.5 mV/s, pH 8, various chloride content).

the scales, its corrosion resistance considerably increased. As a consequence, the second group of points was identified at lower R^2 values and at higher $E_{i=0} - E_{oc}$. The corresponding chloride concentrations do not cause spontaneous corrosion activation.

The subject matter of the paper has been described on the example of martensitic stainless FeCr12 with a bare or scaled surface. As mentioned in the experimental part, other four stainless steels involved in the study gave similar results. The effect of scaling on corrosion resistance is demonstrated also in the case of austenitic stainless steel (Fig. 7). As it could be seen, there are again two more or less separated groups of points, the first of which, containing two symbols for scaled specimens, belongs to the specimens in passive state, and the other, containing four symbols for bare specimens, belongs to the specimens in activity.

Naturally, corrosion activation is associated with a drop of a free corrosion potential which may also be used for distinguishing between the active and passive states. However, the free corrosion potential can be affected by many factors, such as a superficial state, oxygen accessibility, etc. In case that we have no continuous record of the free corrosion potential from the start of exposure in non-carbonated and chloride-free concrete, it would be unreliable to identify the onset of corrosion in active state by means of free corrosion potential. The quantification of non-linearity, as described above, is a useful tool for identification of a real state of corrosion.

4. Conclusions

When a specimen in a passive state is polarized either in cathodic or anodic direction from the free corrosion potential, the zero current potential shows different values on a subsequently scanned linear polarization curve. Non-linearity together with this potential shift causes that the determination of polarization resistance values is unreliable, since the values are underestimated. In some cases, determination of deviation of the polarization curve based on the ideal linear shape is convenient for distinguishing between corrosion in an active or in a passive state. Determination of the polarization resistance by the linear polarization method is unreliable in case of steel in a passive state. With respect to the inaccuracy of R_p, further calculations of corrosion rate by using coefficient B are not reasonable.

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