

Investigations on Cathodic Control of Chloride-Induced Reinforcement Corrosion

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ABSTRACT

There are still contradictions regarding the mechanisms of reinforcement corrosion with respect to the controlling rate-determining factors of the corrosion process. It is often stated that the electrolytic resistance of the concrete is the controlling factor and that the corrosion rates can subsequently be calculated from concrete resistivity. However, extensive research carried out by the authors has clearly demonstrated that instead of concrete resistivity the resistance to cathodic polarisation is normally the controlling factor in the case of chloride-induced macrocell corrosion.

Generally, cathodic control can be related to restricted oxygen diffusion or activation control. In the present paper these relationships are discussed in detail based on results of numerous tests on the cathodic polarisation behaviour of passive reinforcement. For simple defined geometrical conditions simulating practical cases it is shown by a numerical analysis that the resistance to activation is normally the controlling factor for the corrosion rate and that oxygen diffusion has only to be taken into account when the concrete is permanently water saturated or extremely dense.

To verify whether it is correct to estimate corrosion rates from concrete resistivity data, tests should be carried out to check the influencing parameters on concrete resistivity and cathodic activation of passive steel surface areas.

1. Introduction

To evaluate the durability of existing structures and the design for durability of new reinforced concrete structures there is a need to estimate or calculate corrosion rates for specific environmental conditions. Besides complex models based on the electrochemical nature of the corrosion process (see e.g. [1]) simplified models have also been developed which assume that the resistivity of the concrete is the dominating and controlling factor for the corrosion rate of steel in concrete (see e.g. [2]).

However, extensive research on the mechanism of chloride-induced macrocell corrosion of steel in concrete carried out by both authors of this paper has shown that for conditions relevant to actual practice the dominating factor is not the resistivity of the concrete, but the resistance of the passive reinforcement to cathodic polarisation.

In this chapter the basic relationships regarding the mechanism of chloride-induced corrosion are briefly explained to allow the further discussion of the controlling factors, especially the resistance of passive steel to polarisation for combined oxygen diffusion and charge transfer (activation).

2. Electrochemical Background of Macrocell Corrosion

Based on a simplified electrical circuit model [1] the electrical macrocell current, I_{gal} which is proportional to the corrosion rate, can be calculated from the ratio between the driving voltage and the resistances present in the corroding system, using the following basic eqn (1):

$$I_{gal} = \frac{U_{R,c} - U_{R,a}}{\frac{r_c}{A_c} + k \cdot \rho_{con} + \frac{r_a}{A_a}} \quad (1)$$

where

I_{gal}	= galvanic current between anode and cathode	(mA)
$U_{R,c}$	= rest potential of the cathode	(mV)
$U_{R,a}$	= rest potential of the anode	(mV)
r_a	= specific anodic polarisation resistance of the anode	(Ωm^2)
A_a	= anodically acting steel surface area of the anode	(m^2)
r_c	= specific cathodic polarisation resistance of the cathode	(Ωm^2)
A_c	= cathodically acting steel surface area of the cathode	(m^2)
ρ_{con}	= specific resistance of the concrete (resistivity)	(Ωm)
k	= cell constant (geometry)	(1/m)

The resistance of the steel related to the transport of electrons is negligibly small compared to the other resistances in the circuit. The resistances of anode, cathode and electrolyte can again be sub-divided into different partial resistances (see e.g. [3]). The influence of the corrosion cell geometry on the overall concrete resistance is taken into account by the introduction of a cell constant, k .

It is evident that a prediction of the corrosion rate is difficult due to the large number of influencing factors. In addition, the relationships between these factors and the three main resistances are different: water saturation leads e.g. to a low concrete resistivity but a high cathodic resistance (oxygen diffusion control).

The relationships of eqn (1) can be illustrated by a so-called Evans diagram as shown in Fig. 1.

To quantify the control of the resistances, the voltage drops induced by the individual resistances can be calculated and related to the overall driving voltage, U_{oc} , e.g. for the cathodic control part CTRL_c:

$$CTRL_c = \Delta U_c / U_{oc} \times 100 [\%] \quad (2)$$

where ΔU_c = voltage drop induced by the cathodic reaction = $U_{R,c} - U_c$ and U_{oc} = open circuit voltage (driving force) = $U_{R,c} - U_{R,a}$.

The controlling parts of the other two resistances can be calculated analogous to eqn (2).

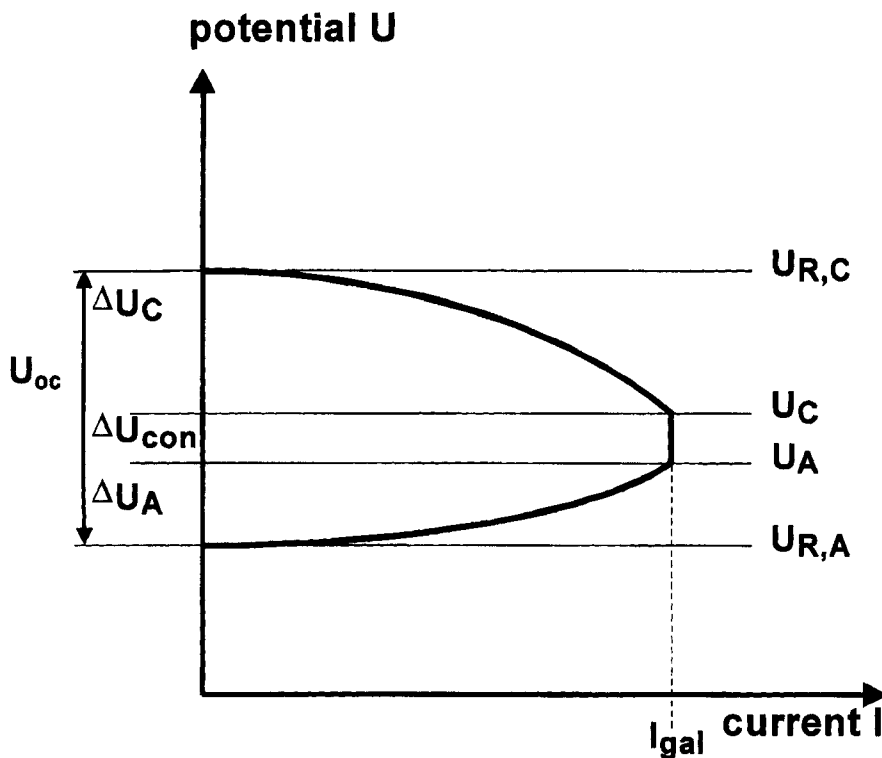


Fig. 1 Evans diagram showing schematically the relationship between voltage and current of a corrosion cell.

Before these controlling factors are calculated for typical macrocells, the influence of oxygen diffusion on the cathodic resistance to polarisation is discussed in the following section.

3. Influence of Oxygen Diffusion and Charge Transfer on the Cathodic Resistance to Polarisation

The voltage drop associated with the cathodic reaction is composed of a charge transfer and a diffusion component, i.e. $\Delta U_c = \Delta U_{c,ct} + \Delta U_{c,d}$. Hence, the overall cathodic resistance to polarisation, $r_{c,r}$ can be divided into two sub-resistances:

$$r_c = r_{c,ct} + r_{c,d} \quad (\Omega m^2) \quad (3)$$

where $r_{c,ct}$ = charge transfer resistance (activation control) and $r_{c,d}$ = diffusion resistance.

The polarisation behaviour of a passive steel surface in concrete can be calculated using the modified equation from the authors of this paper as described in [1] which allows for a discrimination between $\Delta U_{c,ct}$ and $\Delta U_{c,d}$ as follows:

$$i = \frac{1 - \exp\left(\frac{-\ln(10) \cdot \Delta U_c}{b_c}\right)}{\frac{1}{i_{corr}} - \frac{\exp\left(\frac{-\ln(10) \cdot \Delta U_c}{b_c}\right)}{i_{lim}}} \quad (4)$$

For passive steel values of 1.10^{15} mV/dec and 176 mV/decade for the anodic and cathodic Tafel slopes, b_a and b_c respectively, are introduced which results in a Stern-Geary constant $B = 76.6$ mV. The corrosion current density of passive steel at the rest potential, i_{corr} , is set at 0.1 mAcm^{-2} ($0.01 \text{ } \mu\text{Acm}^{-2}$) [1,3,4]. The influence of oxygen diffusion through the concrete cover on the polarisation behaviour is taken into account by introducing a limiting diffusion current density, i_{lim} [3].

For steady state conditions, the limiting current densities for the cathodic reaction can be determined from the oxygen diffusion coefficients based on Fick's first law of diffusion assuming an oxygen concentration of $9.4 \cdot 10^{-6} \text{ mol O}_2/\text{cm}^3$ at the concrete surface and 0 at the steel surface:

$$i_{lim} = 3.63 \cdot 10^{12} \cdot \frac{D_{O_2}}{C_c} \cdot \frac{A_{con}}{A_{st}} [\text{mAcm}^{-2}] \quad (5)$$

where

- D_{O_2} = oxygen diffusion coefficient (m^2s^{-1});
- C_c = concrete cover in (mm);
- A_{con}/A_{st} = surface area ratio between concrete and steel acting cathodically;
 ≤ 1 (reduction factor if the concrete surface is the critical path).

For reinforced concrete structures the surface ratio A_{con}/A_{st} is usually > 1 . For this case the oxygen diffusion near the steel surface is the critical path and the concrete surface area does not play the dominating role with respect to oxygen flow. On the contrary, if the reinforcement density is high, A_{con}/A_{st} may be ≤ 1 and the concrete surface area becomes the critical path resulting in a reduction of the potential limiting cathodic current density as shown in eqn (5).

Figure 2 shows the results from calculations on cathodic behaviour of passive steel using eqn (5) for different oxygen diffusion coefficients, a concrete cover of 80 mm and a surface area ratio of $A_{con}/A_{st} = 0.67$ as an example for a concrete cover with a high resistance to oxygen diffusion. The same results as given in Fig. 2 are shown in Fig. 3 in a modified form by plotting the control part induced by oxygen diffusion with respect to the overall cathodic resistance against polarisation in %.

It is clearly shown, that under these conditions an influence of oxygen diffusion is significant only for oxygen diffusion coefficients below about $10^{-8} \text{ m}^2\text{s}^{-1}$. A considerable influence of concrete cover of the corrosion rate should be expected only for oxygen diffusion coefficients below about $10^{-10} \text{ m}^2\text{s}^{-1}$. According to [5], such low diffusion coefficients in the range of $10^{-10} \text{ m}^2\text{s}^{-1}$ occur mainly in water-saturated concretes.

These calculations show, that in situations where the concrete is not permanently

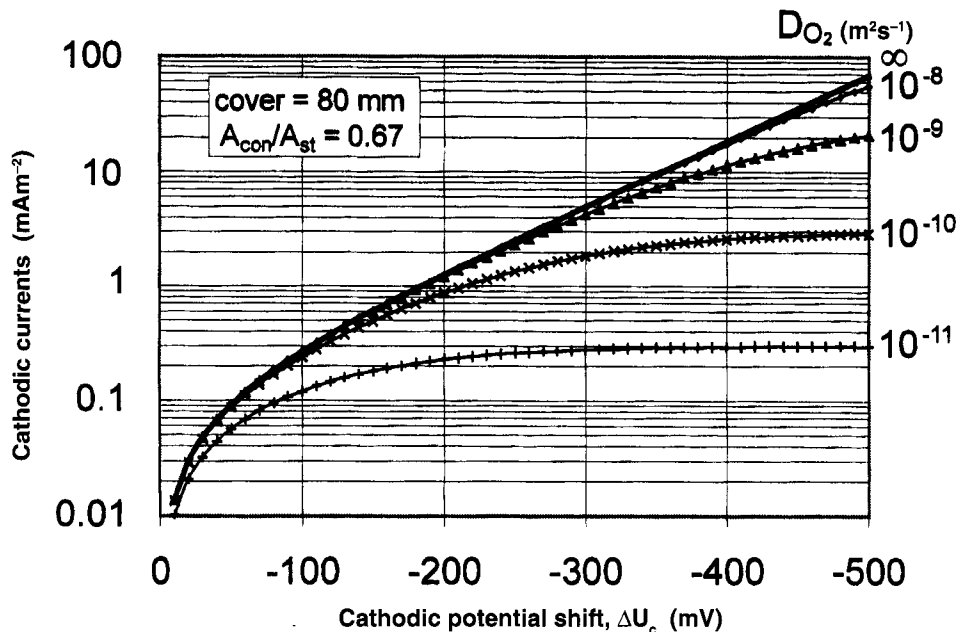


Fig. 2 Cathodic behaviour of passive steel in concrete calculated for different oxygen diffusion coefficients.

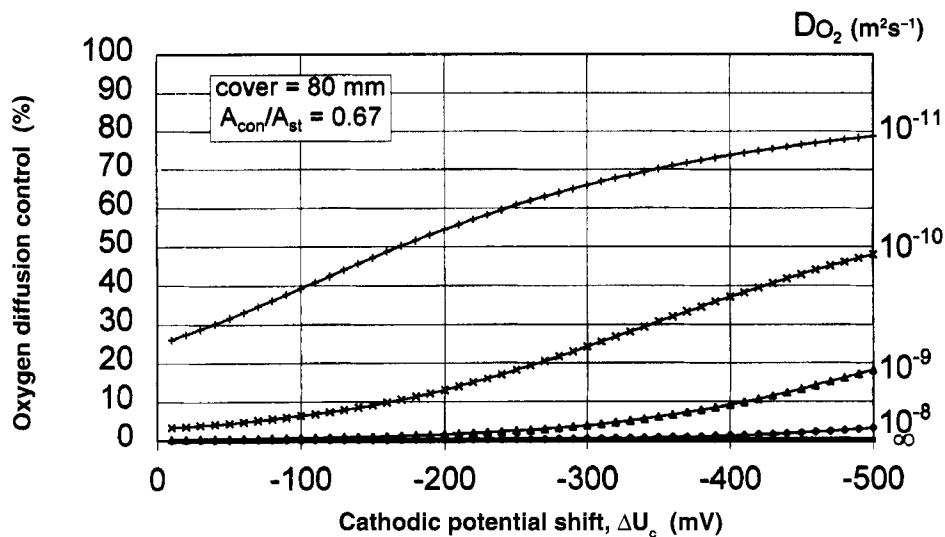


Fig. 3 Influence of the oxygen diffusion coefficients on the cathodic resistance to polarisation of passive steel in concrete (see also Fig. 2).

water-saturated, oxygen diffusion is not a decisive factor influencing the corrosion rate of the reinforcement directly. On the other hand, the cathodic charge transfer resistance is not negligible.

4. Numerical Simulation of Macrocells with Planparallel Arrangement

The control exerted by the anodic, electrolytic and cathodic processes on the electrochemical behaviour of a macrocell was investigated by using a numerical simulation model. This mathematical analysis is based on the electrochemical relationships between current and potential as outlined in the foregoing. For simplicity, a planparallel arrangement of two separate steel plate electrodes representing a variable number of steel bars is considered placed on the top and bottom surface of a concrete specimen, respectively (see Fig. 4).

The steel/concrete interface of the top electrode is considered to be actively corroding whereas the interface of the bottom electrode remains essentially passive. The potential difference between corroding and passive steel serves to provoke a so-called active/passive macrocell with the corroding steel acting as the overall anode and the passive steel as the overall cathode. The resulting electrochemical interaction may have a pronounced accelerating effect on the corrosion rate of the anodic component of the macrocell couple. This situation is designed to simulate actual conditions of galvanic corrosion, e.g. the cross section of a bridge or parking deck suffering from chloride penetration from the top concrete surface. The ensuing corrosion process is stimulated by the passive steel rebars at the bottom surface which remain essentially passive.

The concrete specimen is given a cross section, measuring $400 \times 200 \text{ mm}^2$, and a unit depth of 1000 mm. The width of the passive and corroding steel electrodes (depth of 1000 mm) can be adjusted to vary the surface area ratio P/A . In this numerical simulation the ratio is increased in a stepwise fashion from 0.04 to 25.

As a starting point for the numerical simulation, the initial corrosion current density of the corroding steel surface, denoted A , due to microcell action is arbitrarily set at $i_{\text{corr}} = 10 \text{ mAcm}^{-2}$ ($1.0 \text{ } \mu\text{Acm}^{-2}$) (self-corrosion rate). The corresponding polarisation

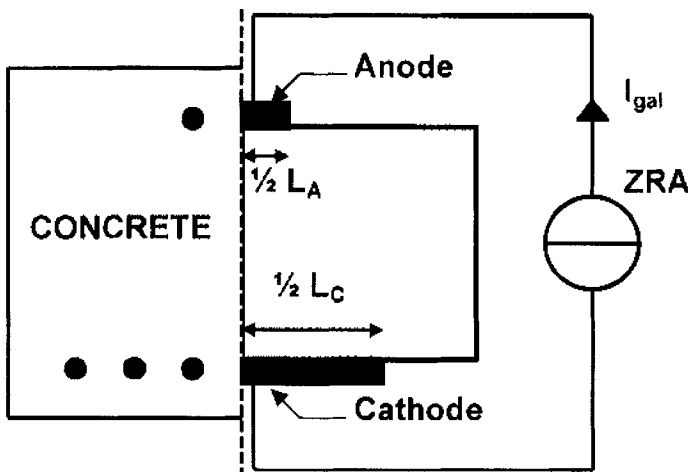


Fig. 4 Cross-section of a reinforced concrete compound and modelling using a macrocell specimen with planparallel steel plate electrode arrangement (unit depth: 1000 mm).

behaviour is characterised by anodic and cathodic Tafel constants, $b_a = 91$ mV/decade and $b_c = 176$ mV/decade, respectively, resulting in a Stern–Geary constant $B = 26$ mV [2].

For the passive component, denoted P , the initial corrosion current density is set at $i_{corr} = 0.1$ mA m^{-2} (0.01 μA cm^{-2}). The polarisation behaviour is described by $b_a = 1 \cdot 10^{15}$ mV/decade and $b_c = 176$ mV/decade, reflecting ideal passive behaviour (corrosion current density remains at a constant negligible value).

For both electrodes the influence of limited oxygen diffusion on the cathodic processes is not taken into account since this situation is considered to be of practical relevance only for prolonged submerged conditions [3]. Throughout the numerical simulations the driving voltage between the cathodic and anodic component is fixed at $U_{oc} = 500$ mV. The influence of the electrolytic resistivity of the concrete body of the specimen, $\rho_{con'}$ on macrocell action was investigated for $\rho_{con} = 50, 100$ and $500 \Omega m$ (see Fig. 6).

The electrochemical behaviour of the steel/concrete interface is modelled by discrete equidistant interface elements of 2 mm width (1000 mm depth). The electrolytic properties of the concrete material are modelled by pure resistive elements each representing a square cross section of 2×2 mm² (1000 mm depth). For practical reasons the numerical analysis is used to calculate the electrochemical potential and current distribution in a two-dimensional situation under steady state conditions. The macrocell current, $I_{gal'}$ is measured by a so-called Zero Resistance Ammeter (ZRA), inserted in the external part of the equivalent electrical circuit. Since the method is capable of calculating the anodic and cathodic currents, the accelerating effect of macrocell action on the corrosion rate can be quantified.

The control exerted by the anodic, electrolytic (concrete) and cathodic processes on the electrochemical behaviour of the macrocell is defined according to eqn (2). The voltages ΔU_a and ΔU_c correspond to the shift in potential of the anodic and cathodic component, respectively, relative to their respective initial free corrosion potential. The voltage U_{con} refers to the voltage drop over the concrete electrolyte induced by the flow of the macrocell current between the anodic and cathodic component.

In Fig. 5(a) and 5(b) the development of the control is depicted as a function of surface area ratio P/A for $\rho_{con} = 50$ and $100 \Omega m$, respectively. As the ratio P/A increases from 0.04 to 25 the cathodic control decreases gradually from 93% to 61% ($\rho_{con} = 50 \Omega m$) and from 90 to 56% ($100 \Omega m$). Simultaneously, the anodic and electrolytic control increase from 1 and 6% to 20 and 19% respectively ($\rho_{con} = 50 \Omega m$), and from 1 and 10% to 18 and 26%, respectively ($\rho_{con} = 100 \Omega m$).

This demonstrates that the influence of the cathodic process on macrocell behaviour can be very pronounced. Especially for small ratio values the cathodic process forms the major portion of the total macrocell circuit resistance. However, it should be borne in mind that the electrolyte resistance is influenced by the P/A ratio and the geometrical constraints of the selected specimen.

The accelerating effect of macrocell action on the corrosion rate of the anodic component is demonstrated in Fig. 6 for $\rho_{con} = 50, 100$ and $500 \Omega m$. The corrosion current density, i_a' , including macrocell effects, is given as a function of surface area ratio P/A . As the ratio P/A increases from 0.04 to 25 the corrosion rate is increased considerably by 11.8 to 1241% for $\rho_{con} = 50 \Omega m$, by 9.3 to 864% for $\rho_{con} = 100 \Omega m$ and

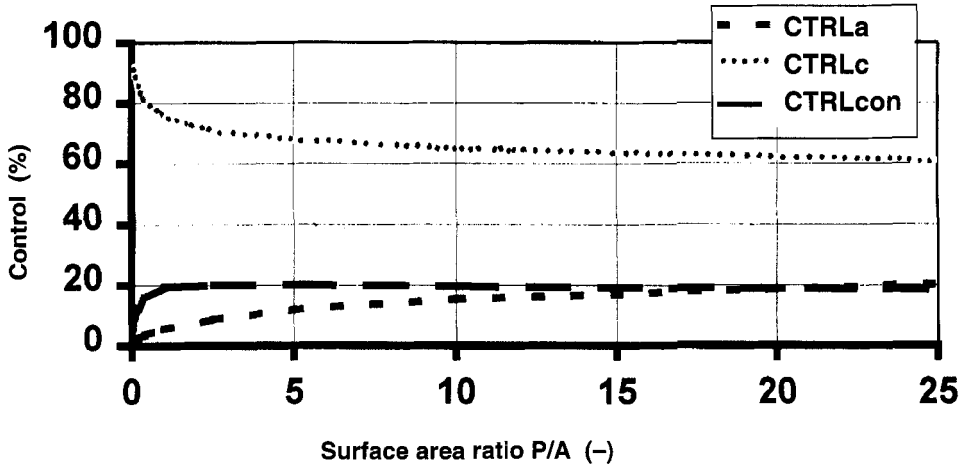


Fig. 5(a) Development of control exerted by macrocell components as a function of surface area ratio P/A : $\rho_{con} = 50 \Omega m$.

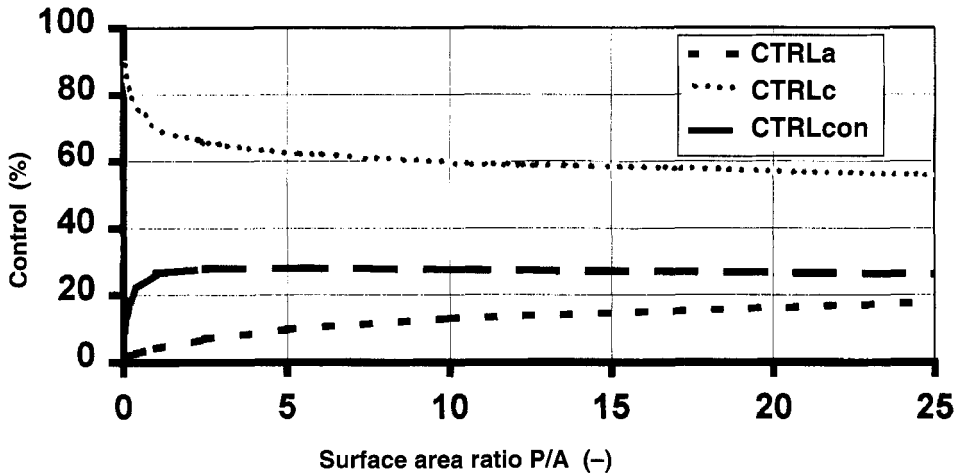


Fig. 5(b) Development of control exerted by macrocell components as a function of surface area ratio P/A : $\rho_{con} = 100 \Omega m$.

by 4.2 to 291% for $\rho_{con} = 500 \Omega m$. Generally, the galvanic current, I_{gal} underestimates the actual corrosion rate, but for high values of P/A this may give reliable information on the magnitude of the corrosion process of the anodic component.

In addition, active-passive macrocells normally result in a strong cathodic polarisation of the passive steel. In Fig. 7 this effect is illustrated for $P/A = 25$ ($L_c = 100$ mm and $L_A = 4$ mm) by the equicontour plot of potentials in the concrete between anode and cathode.

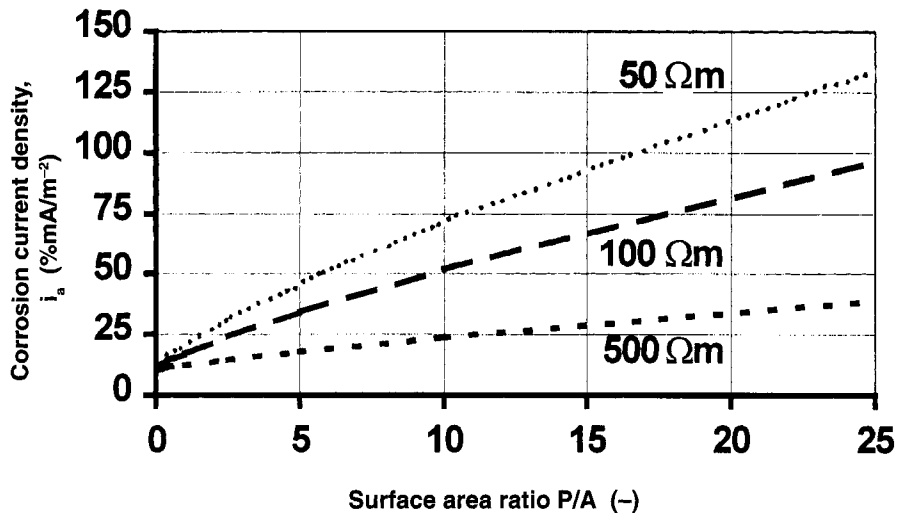


Fig. 6 Development of corrosion current density of anodic component as a function of surface area ratio P/A.

5. Discussion and Concluding Remarks

It is generally accepted that macrocell action plays an important role in the corrosion process of reinforcement steel embedded in concrete. Normally, oxygen diffusion and concrete resistance are considered to dominate the magnitude of macrocell action under most practical conditions. However, this view is based on implicit assumptions rather than objective quantitative information. Hence, there is a potential need for research addressing this subject.

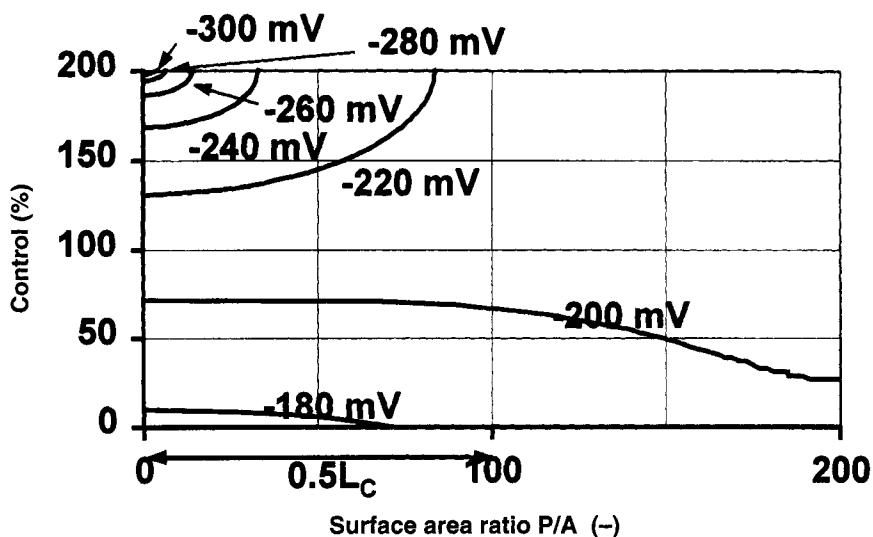


Fig. 7 Equipotential plot for P/A = 25 (for explanations, see text).

Based on the electrochemical nature of reinforcement corrosion, the behaviour of corroding and passive steel can be described by relationships between current and potential. These mathematical expressions allow a distinction to be made between activation (charge transfer) and oxygen diffusion controlled processes. For most practical conditions, oxygen diffusion is not considered to be of importance except when exposed to continuous or prolonged water immersion. This finding is supported by the results presented in [6].

For a macrocell the total circuit resistance can be regarded as a connection of three resistances in series, viz. a resistance associated with the anodic, electrolytic, and cathodic components, respectively. However, most practical situations will not allow a quantitative distinction between these resistances to be made. Hence, the relative importance of these components on the overall macrocell behaviour cannot be easily evaluated. This problem can be overcome by a numerical simulation of the relevant electrode and electrolytic processes.

The current–potential relationship for the cathodic and anodic processes can be simulated by introducing discrete non-linear resistive elements for the steel/concrete interface. These elements represent the resistance to polarisation of passive and corroding steel, respectively. The ionic pathway between the anodic and the cathodic component of a planparallel macrocell arrangement can be modelled by using pure resistive elements. The numerical method is applied to simulate a situation known to be occurring in practice with distinct spatial separation between corroding and passivated reinforcement steel.

The surface area ratio between passive and corroding steel, P/A , is varied in a stepwise fashion intended to cover the range of practical importance for two values of concrete resistivity (50 and 100 Ωm).

The results of the numerical simulation clearly demonstrate that for small values of P/A the resistance to polarisation of the passive steel is the main contributor to the overall macrocell resistance. This can be explained by the fact that in contrast to actively corroding steel passive steel exhibits a high resistance to polarisation. Considering equal surface area, passive and corroding steel correspond to resistances of 765 and 2.6 Ωm^2 respectively (at the free corrosion potential). These values only apply to the specific values of the electrochemical factors used in this stimulation. The resistance values decrease as the change in potential increases and as the surface area increases. Therefore the three resistances involved are very much dependent on geometrical factors. As the surface area ratio P/A increases, the resistance to polarisation of the passive steel component decreases and hence its relative contribution to the overall macrocell resistance. Nevertheless, for $P/A = 25$ approximately 60% of the circuit resistance is attributable to the passive steel. However, the contribution of the corroding steel component always remains limited to less than 20%. This situation is largely due to the high initial corrosion current, I_{corr} . In general, the resistance to polarisation is inversely proportional to I_{corr} .

The results of the numerical simulation also clearly demonstrate that corrosion can be seriously aggravated by the presence of macrocells. According to [7] the corrosion rate is hardly affected by the presence of macrocells. However, this conclusion is only based on laboratory experiments with $P/A = 1.0$. From the present numerical simulation it is clear that the corrosion current density, i_a , i.e. the rate of attack, is strongly influenced by the surface area ratio P/A .

6. Outlook

In view of the practical importance of reinforcement corrosion, further experimental research is urgently needed to validate the results obtained by a numerical analysis. Especially, investigations on the effect of cathodic charge transfer at the steel / concrete interface under different exposure conditions and for a range of concrete qualities may improve the model and its practical use.

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