

## **In-situ monitoring of the efficiency of the cathodic protection of reinforced concrete by electrochemical impedance spectroscopy (EIS)**

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### **1. INTRODUCTION**

The reinforcement in concrete is usually in a state of passivity due to the high alkalinity of the pore solution. However, reduction of the pH due to carbonation or especially the ingress of chloride ions into the concrete structure from deicing salt application may induce severe corrosion of the rebars, leading to the deterioration of the structure. The need for the repair of corroding concrete structures was growing rapidly during the past decade.

The corrosion of rebars in concrete is due to electrochemical processes which are governed principally by local potential differences on the rebars, oxygen concentration and humidity. If the local rebar potential drops below the "passive state" either by the reduction of the pH through carbonation of the alkaline-buffer calcium hydroxide or if the passive layer is destroyed by chloride ingress, then corrosion will start if sufficient humidity and oxygen is present. The currently most widely used repair techniques focus on the repair of the concrete overlay. However, these concrete repair methods may create potential differences between the repaired and the adjacent non treated areas initiating corrosion in the adjacent non-treated areas. Another approach for controlling rebar corrosion focuses on the regulation of the electrochemical potential of the rebars through cathodic polarisation by an external power source. Cathodic protection of reinforced concrete structures is a widely employed method in the U.S. and is becoming increasingly accepted in Europe [1]. The efficiency of the cathodic protection is evaluated by purely empirical criteria, the 100 mV depolarisation- or the  $E/\log(I)$  - criterion [2]. However these criteria do not allow an assessment of actual changes of the state of the rebar surface during polarisation.

In the present work the technique of electrochemical impedance spectroscopy (EIS) was evaluated for monitoring the change of the rebar status at various times of applied cathodic protection in concretes containing different amounts of chloride. A simple method principally proposed by Haruyama et al. [3] using two selected AC-frequencies was developed to observe the change of the corrosion state and the results were verified by linear polarisation resistance (LPR) measurements.

### **2. BACKGROUND**

A schematic representation of the mechanism of chloride induced rebar corrosion is given in figure 1 [4]. During the corrosion process an electric corrosion current flows from the local areas where rust is formed (anode) to the local areas where oxygen is transformed into water (cathode). The anodic and cathodic areas occur as a result

of coupling dissimilar metals and/or exposure to differential environmental conditions [2][5].

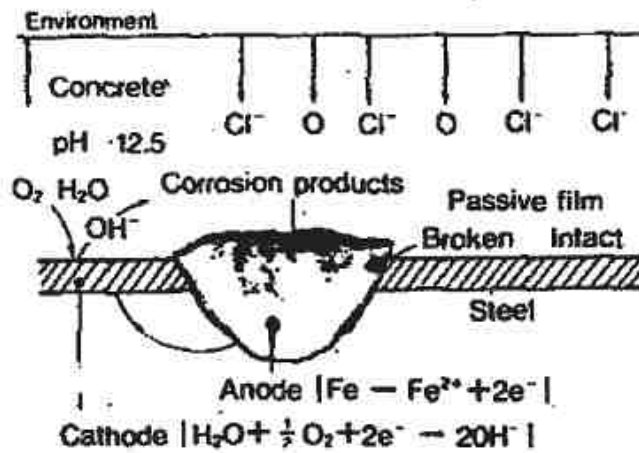


Figure 1: Model for corrosion within concrete from reference 4

The driving force of the corrosion is the potential difference between the anodic and cathodic reaction. Therefore, the probability of corrosion may be estimated by determining the local equilibrium potential of the rebar. This is usually done by potential mapping of the surfaces of concrete structures [6]. Potential mapping is a very useful non-destructive technique for delineating the areas of corrosion, however, it allows no direct assessment of the corrosion rates and the potentials cannot always be interpreted in a straightforward manner, especially in the intermediate ranges [7].

The corrosion rates may be estimated from the determination of the charge transfer resistance  $R_{ct}$ . The corrosion current is inversely proportional to  $R_{ct}$  and the ohmic resistance of the pore-solution electrolyte  $R_{\Omega}$  (Eq. 1) [8-9].

$$\text{Equ. 1} \quad i_{corr} = \frac{B}{R_P} \quad R_P = R_{\Omega} + R_{ct}$$

$B$  is the polarisation resistance constant, which may be determined from the Butler-Volmer relationship [10]. As the distance between anodic and cathodic areas is usually small,  $R_{\Omega}$  may be neglected.  $R_p$  is usually determined by linear polarisation measurements (LPR).  $R_{\Omega}$  in LPR-measurements corresponds to the ohmic resistance of the concrete overlay which is usually in the order of  $R_{ct}$ .  $R_{\Omega}$  depends on the pore-solution composition and the concrete porosity which might vary over time significantly.  $R_{ct}$  may also be determined by galvanostatic pulse measurements [7] or by EIS [11-13].  $R_{ct}$  determined by galvanostatic pulse measurements varies with the ohmic resistance of the concrete overlay [7] whereas  $R_{ct}$  determined by EIS is purely a function of the state of the rebar surface/pore-solution interface. If the ohmic resistance of the concrete overlay is sufficiently large, which is usually the case, then EIS measurements allow an unambiguous assessment of the state of the local corrosion of rebars in concrete [12].

The technique of cathodic corrosion protection is based on the potential dependence of the corrosion current [2]. By applying a voltage by an external power source between the rebars and an anode placed on the surface of the concrete structure, the potential of the rebars is shifted towards negative values. The cathodic polarisation results in a reduction of the corrosive anodic current and in an increase of the cathodic current (figure 2). Oxygen instead of being reduced by the corroding rebar-iron is then principally reduced by the supplied cathodic protection current.

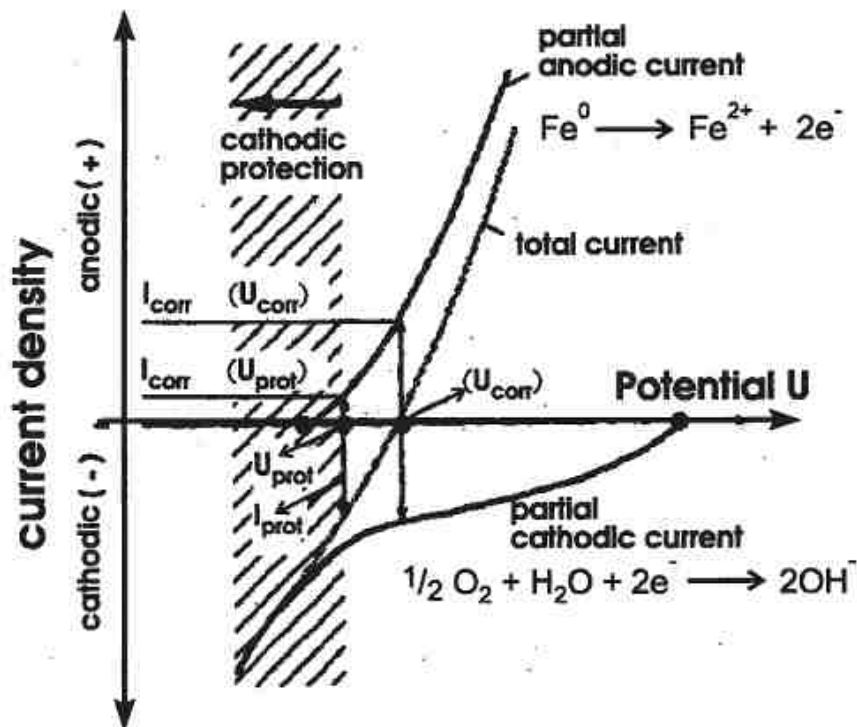


Figure 2: Potential dependence of the anodic, cathodic partial and the total current densities for uniform corrosion. At equilibrium, the total current is zero. Cathodic polarisation results in an increase of the cathodic partial current on the expense of the corrosive anodic partial current. The cathodic total current  $I_{prot}$  is supplied by the external power source. (from reference 14)

According to NACE [2], cathodic protection is the only proven procedure currently available to control corrosion of steel in existing chloride contaminated concrete structures. The cathodic protection techniques differ mainly by the type of anode material placed on the surface of the concrete structure. Two principal types of anode-materials are used: Titanium-mesh anodes and conductive coating anodes [1]. The significant advantages of conductive coatings are that, being a coating, it can be applied to complex shapes in any orientation and presents no problems of weight or dimensional limitations. In addition, conductive coating systems can be installed onto suitable structures at approximately half the cost of alternative distributed anode systems which require substantial overlays. Conductive coatings thereby avoid possible cementitious overlay disbondment problems [1]. Most conductive coatings are skeleton conductors. The conducting skeleton consists usually of graphite particles incorporated into acrylic resin. The mechanical stability is reduced due to the required high graphite content and ageing

may lead to the disruption of the graphite particle skeleton reducing the conductivity. In this work, a graphite containing intrinsic conductive polymer coating was used as anode material. This material is used successfully by Coating Int. A.S. in Norway and the Netherlands as an "active paint - system" combining protective coating with corrosion protection by cathodic polarisation of the rebars (figure 3).

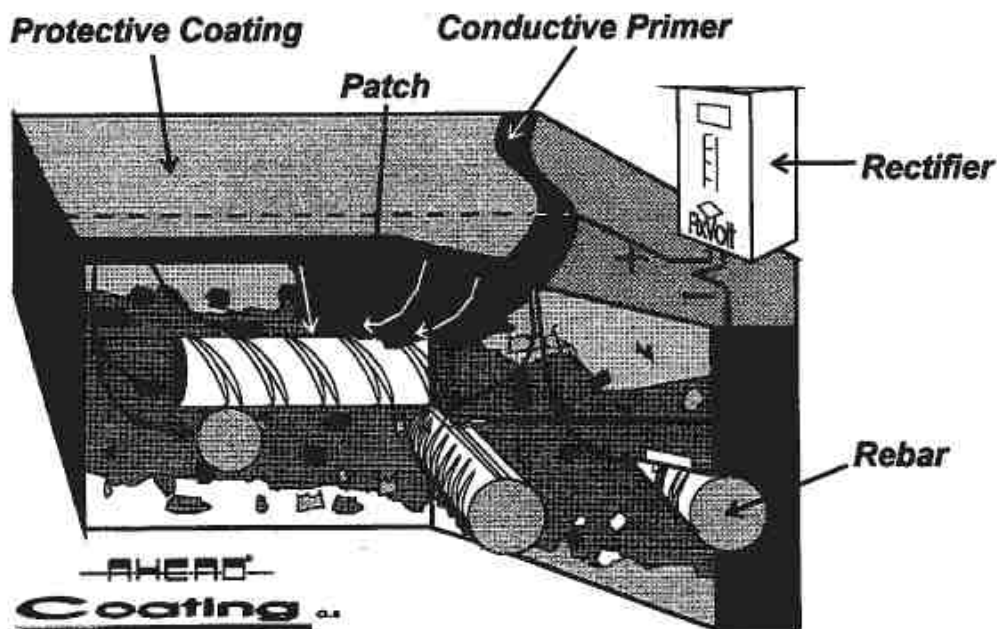


Figure 3: Active paint system combining protective coating with corrosion protection by cathodic polarisation (with the permission of Coating Int. A.S.)

### 3. MATERIALS AND EXPERIMENTAL PROCEDURES

Two sets of experiments were executed:

Linear polarisation measurements (LPR), full-scale EIS - and EIS-measurements at two fixed frequencies were executed on steel bars in dilute sulfuric acid and in simulated concrete pore-solutions with and without chloride. Following the work of Wenger and Galland [12], the steel bar (8 mm diameter, 50 cm long) was composed of two stainless steel rods with a mild steel (rebar quality) in the middle section, forming a corrosion macro cell with the stainless steel rod as cathode and the mild steel as anode. EIS and LPR measurements were carried out with  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4\text{sat}$  reference electrodes in dilute sulfuric acid and a  $\text{Hg}/\text{HgO}$  reference electrode in alkaline simulated pore solutions with a Pt-wire as counter electrode by moving the arrangement of the counter and reference-electrode from measuring point to measuring point parallel to the bar at a distance of 1 cm. Details are described elsewhere [15].

Linear polarisation measurements (LPR) and EIS-measurements at two fixed frequencies were executed on mortar prisms ( $10 \times 10 \times 50$  cm) before and after various times of cathodic polarisation of the embedded rebar. Reinforcing steel rods with a diameter of 8 mm were axially positioned within the prisms. The mortar was prepared with a water/cement ratio of 0.5 and  $300 \text{ kg cement}/\text{m}^3$  and with different chloride content (0%, 1%, 2% and 3%) added as NaCl with the mixing water. Into the wet mortar prisms 8 graphite electrodes (each 3 cm long) were embedded every 10 cm, 4 on both sides of the steel bar with a distance of about 5 mm. The mortar prisms were cured for 28 d at room temperature at  $> 90\%$  r.H. After curing a conductive coating (from Coating Int. A.S.) was applied on one side of the prism. Electric connections were made with silver tapes. For cathodic polarisation, a voltage of 2 V was applied generating a polarisation current in the range of  $20 - 500 \mu\text{A}/\text{cm}^2$  rebar surface depending on the chloride content. EIS- and LPR-measurements were carried out with a couple of graphite electrodes, one serving as a reference and the other as a counter electrode. The EIS- and LPR-measurements are described elsewhere in detail [15].

#### 4. RESULTS AND DISCUSSION

For the determination of  $R_{\Omega}$  and  $R_{ct}$  by EIS the same model as by Wenger and Galland [12] was used. The determination of  $R_{\Omega}$  and  $R_{ct}$  at two fixed frequencies was validated by EIS-measurements on steel-macro elements in 0.1N sulfuric acid [15]. The relaxation time constant  $\tau_0$  of rebars in the simulated pore solution (saturated  $\text{Ca}(\text{OH})_2$ , 20 mmol  $\text{CaSO}_4$ ) and in concrete is in the order of 1000 s, too high for recording the impedance over the full frequency range for obtaining a full Thales circle on the Nyquist impedance plot. The  $R_{ct}$  values obtained on macro-elements in 0.1N sulfuric acid from EIS correlate linearly with the  $R_{ct}$  values obtained from the impedance determined at 2-frequencies (200 Hz, 10 Hz) with a slope  $s = 0.47$  and an intercept  $i = 0.19$  ( $r^2 = 0.92$ ) (equ. 2) [15]:

$$\text{Equ. 2: } R_{ct}(f_1, f_2) = s * R_{ct}(\text{real}) + i$$

In the simulated pore solution, the 2-frequency (1125 Hz, 0.25Hz)  $R_{ct}$  values correlated with the  $R_{ct}(\text{real})$  values with a slope of 0.19 and an intercept  $i = 0.78$  ( $r^2 = 0.999$ ). The  $R_{ct}$  values obtained by EIS were also compared with the polarisation resistance values  $R_p$  (Equ.1) obtained by LPR-measurements. In solution,  $R_{\Omega}$  is small compared with  $R_{ct}$ , the  $R_p$  values should correspond to the  $R_{ct}$  values determined by EIS. This is the case as shown in figure 4.

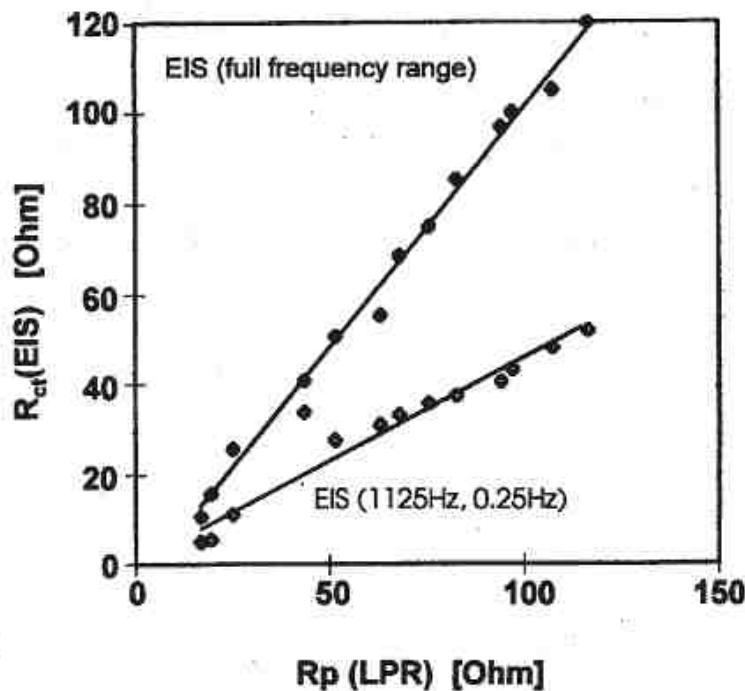


Figure 4: Correlation of  $R_{ct}$  values obtained by EIS and EIS at two frequencies with  $R_p$  values obtained by LPR-measurements of steel macro elements in a simulated concrete pore solution (sat.  $\text{Ca}(\text{OH})_2$ , 20 mmol  $\text{CaSO}_4$ ).

$R_{ct}$  values obtained by 2-frequency EIS correlate also linearly with  $R_p$  values obtained by LPR-measurements on rebars in a simulated pore-solution with different chloride contents (chloride added as  $\text{CaCl}_2$ ) as shown in figure 5.

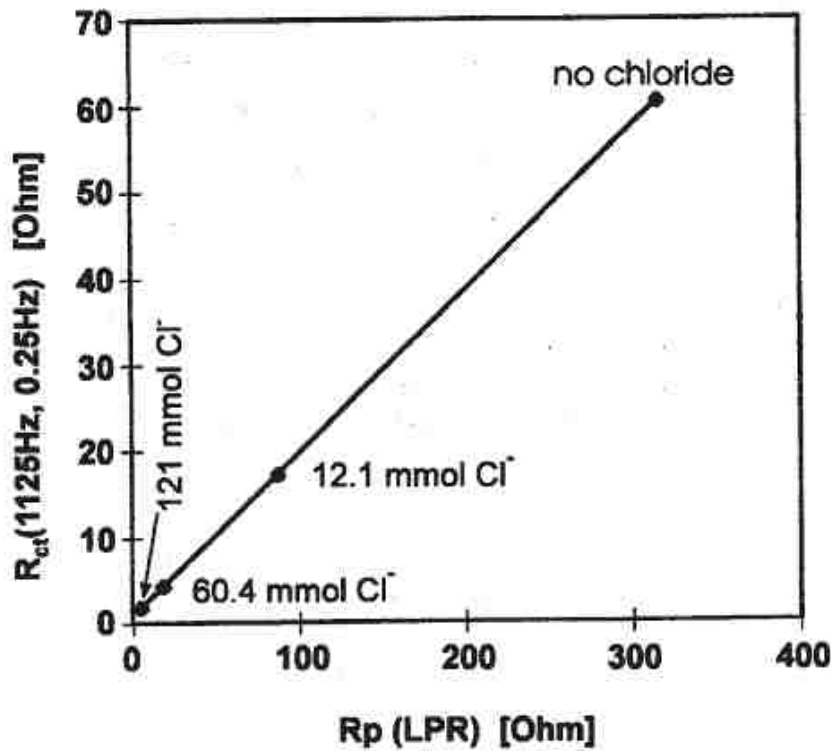


Figure 5: Correlation of  $R_{ct}$  obtained by EIS-at two frequencies (1125, 0.25 Hz) with  $R_p$  values from LPR-measurements on a rebar in a simulated pore solution (sat.  $\text{Ca}(\text{OH})_2$ , 20 mmol  $\text{CaSO}_4$ ) with different chloride contents.

Figure 6 shows the correlation of  $R_{ct}$  values obtained by EIS at two frequencies (1000 Hz, 0.25 Hz) with  $R_p$  values corrected for  $R_\Omega$  obtained by EIS at 1 kHz in concretes with different chloride contents.

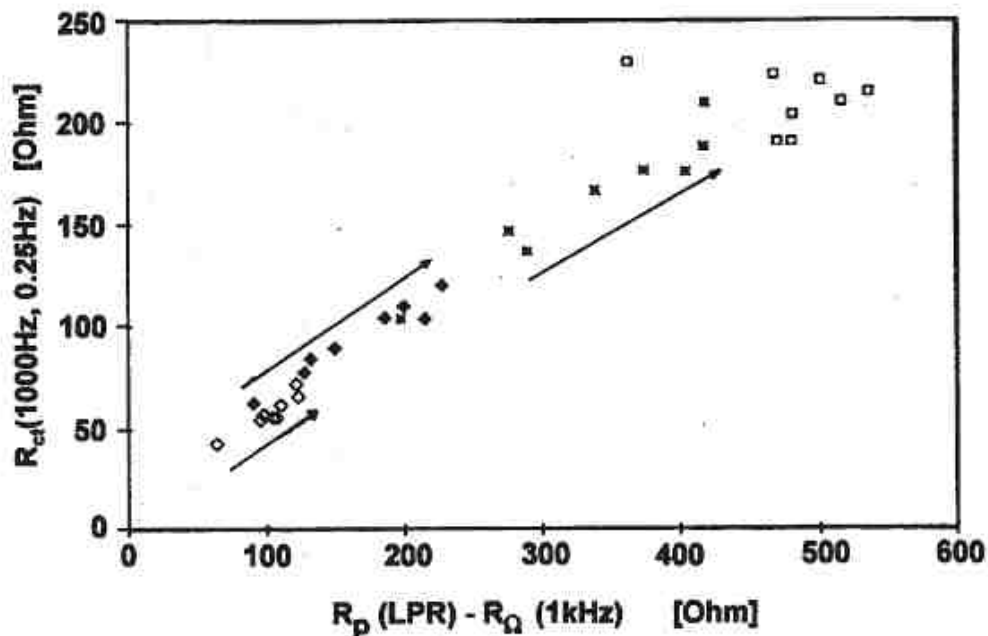


Figure 6: Correlation of  $R_{ct}$  obtained by EIS-at two frequencies (1125, 0.25 Hz) with  $R_p$  values from LPR-measurements corrected for  $R_\Omega$  in concrete with different chloride contents.

◇ 0% chloride      \* 1% chloride      ◆ 2% chloride

For the comparison of  $R_p$  values with  $R_{ct}$  obtained by two-frequency-EIS in concrete, the  $R_p$  values have to be corrected for the ohmic resistance of the concrete overlay.

The results show, that there is a linear correlation of the actual charge transfer resistance values on rebars in concrete with the  $R_{ct}$  values obtained by EIS measurements at two fixed frequencies. The absolute  $R_{ct}$  values determined by the 2-frequency method differ from the actual  $R_{ct}$  values but for the evaluation of the change of the rebar status during corrosion or during cathodic protection, the determination of the change of the  $R_{ct}$  values is sufficient.

In figure 7, relative corrosion rates, calculated from  $R_{ct}$  values determined by 2-frequency EIS are plotted against the charge consumed during cathodic polarisation. In concrete containing 2% of chloride,  $R_{ct}$  values increase as a result of cathodic polarisation whereas in chloride free concrete, there is no significant change of the corrosion rate respectively the  $R_{ct}$  values. This is in agreement with the expectation that the corrosion rate of passivated rebars should not change during cathodic polarisation.

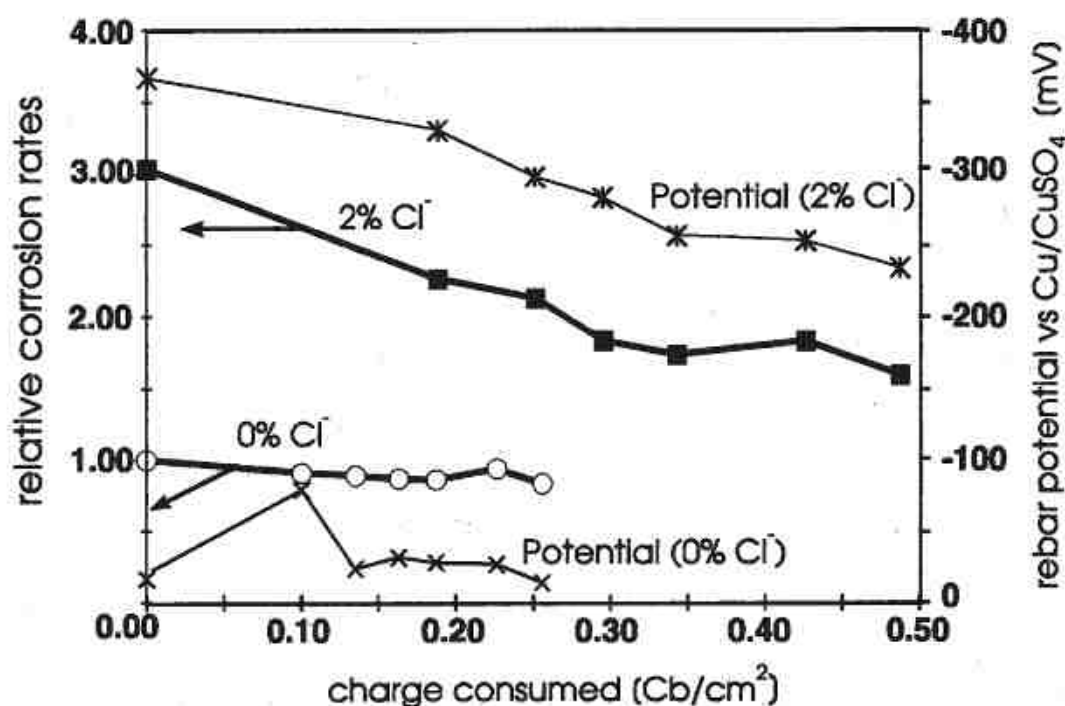


Figure 7: Influence of cathodic polarisation (47 days) on the relative corrosion rates calculated from EIS-2-frequency  $R_{ct}$  - values and on the equilibrium potential. Both parameters were measured 24 h after turn off of the cathodic polarisation voltage.

The increasing  $R_{ct}$  values respectively decreasing corrosion rates as a result of cathodic polarisation indicate that the rebars are partially repassivated either by chemical changes near the rebar/pore solution interface, e.g. electro-osmotic chloride removal or eventually by changes on the rebar surface itself.

## 5. CONCLUSIONS

Relative changes of the charge transfer resistance  $R_{ct}$  may be determined by EIS at two selected frequencies. This measurement technique allows the characterisation of a large number of corroding areas in a fast and efficient way and can be used for monitoring the effectiveness of cathodic protection systems also in large installations.  $R_{ct}$  values of rebars in chloride contaminated concretes increase as a result of prolonged cathodic polarisation.

### Acknowledgement:

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