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IN-*SITU* MONITORING OF THE EFFICIENCY OF THE CATHODIC PROTECTION OF REINFORCED CONCRETE BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Abstract—In the course of applying cathodic protection on concrete structures exposed to chloride contamination (sea-water or de-icing salt), characterization of the effectiveness of the protection procedure is a most important point. This effectiveness is related with the removal of aggressive ions and with the rebuilding of the passive layer on the steel surface. The measuring-procedure applied until now is based on the measurement of the change with time of the potential difference between the reinforcement and (normally embedded) reference electrodes after switching off the protection current. The criterion defined by NACE (National Association of Corrosion Engineers) for a sufficient working of a cathodic protection installation is based on empirically evaluated values. The workability of an improved cathodic protection equipment, using recently developed anodic materials[1], was monitored by impedance spectroscopic techniques. A strong dependence of the charge transfer resistance (R_{ct}) values of the corrosion reaction on the cathodic charge consumed during the protection procedure was found. Results from linear polarization and corrosion potential measurements are well comparable with the impedance data. The main advantage of the impedance technique is the capability of a fast and automatic measuring procedure and of the possibility of on-line monitoring.

Key words: reinforcement corrosion, cathodic protection, corrosion monitoring, impedance spectroscopy, linear polarization measurement.

INTRODUCTION

Concrete is an ideal environment for steel due to its high alkalinity (pH = 12–13.5). Passivity of the embedded steel is the result. Therefore, reinforcing steel in most concrete structures is not subjected to corrosion processes. However, when aggressive substances like carbon dioxide or chloride ions penetrate the concrete structure and reach the steel rebars, corrosion can start. The corrosion products (rust) take up a larger volume than the iron, developing high pressures within the concrete. The adhesion between concrete and rebars will decrease and cracking or spalling of parts of the concrete starts. Ultimately, destruction of the building occurs and major repair or replacement is needed.

Contamination by chloride ions is the primary reason for corrosion of steel reinforcement in concrete. Various sources like de-icing salt, seawater or hardening accelerators $(CaCl_2)$ deliver the chloride ions.

Corrosion can be eliminated by preventing aggressive ions from entering the concrete or coming in contact with the rebar. On new structures this can be done by using, protective coatings. However, on existing structures where chlorides have already accumulated in the concrete, such coatings for the repair of a corroding structure are useless.

"The only rehabilitation technique that has proven to stop corrosion in salt-contaminated bridge decks regardless of the chloride content of concrete is cathodic protection[2]".

The use of cathodic protection (CP) of reinforced concrete to stop or to reduce corrosion drastically is accepted today by most people in the concrete rehabilitation industry. However, disagreement still exists on the methods used to measure the effectiveness of a CP system. A variety of CP criteria have been proposed, including those using electrode operating potential, potential shift, potential decay, potential-current relationship and a statistical treatment of static potentials[3].

Most of these techniques have been adapted from their use in CP-systems applied in underground or submerged structures and have not been rigorously verified for application in concrete. Verification is particularly difficult since direct observation of the amount of corrosion occurring on steel rebars is not easy realizable.

The "depolarization criterion", requiring a potential decay of at least 100 mV in a period of 4 h, is at this time the most widely used one, but uncertainties still exist in using and interpreting the measured data[4, 5].

Different groups have used impedance spectroscopy for the characterization of the corrosion behaviour of steel in concrete[6–10].

In the present work the technique of impedance spectroscopy was used to get information about the

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change of the rebar status in concrete samples with different amounts of chloride ions after various times of applied CP. A simple method principally proposed by Haruyama et al.[11] using two selected ac-frequencies was developed to observe the change of the corrosion state and the results were verified by linear polarization resistance (LPR) measurements.

MATERIALS

Steel bar in sulfuric acid

A stainless steel bar (8 mm in diameter, 50 cm long) with a small mild steel rod in the middle dipped in 0.1 N H_2SO_4 was used as a model system. The experiments carried out for the investigations of the occurrence of local corrosion follow the work of Wenger and Galland[12]. In the sulfuric acid solution the mild steel is active and forms a corrosion macrocell with the stainless steel.

To simulate practical monitoring conditions, the impedance measurements were carried out with a reference electrode ($Hg/Hg_2SO_4/K_2SO_{4\,sat.}$) and a counter electrode (Pt wire) kept close to each other and the dimensions of the counter electrode were small in comparison to the length of the bar.

Impedance measurements were performed by moving the arrangement of the counter and reference electrode from one measuring point to another measuring point parallel to the bar at a distance of 1 cm (Fig. 1).

Reinforced mortar beams

Impedance measurements have been carried out on small mortar prisms (10 × 10 × 50 cm). Reinforcing steel rods with a diameter of 8 mm were axially positioned within the prisms giving a minimum of 40 mm cover of concrete. The mortar/air/steel interface was insulated with a shrink tube. The mortar specimens were made with a water/cement ratio of 0.5. A content of ordinary portland cement of 300 kg/m³ was used. Prisms with a content of 0%, 1%, 2% and 3% chloride/cement weight were prepared (chloride was added as NaCl in 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 at a distance of about 5 mm (Fig. 2). After casting, the samples were covered with a polyethylene foil to ensure high humidity during the curing time (28 days) at ambient temperature.
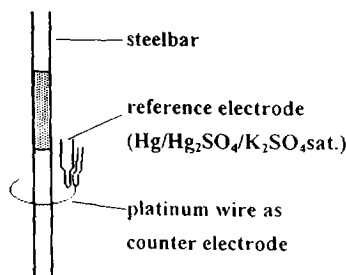

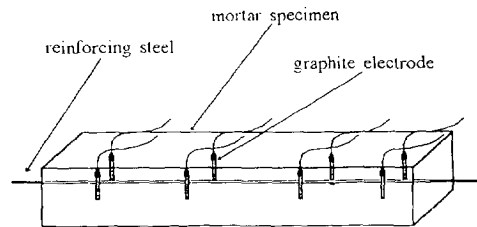Fig. 1. Arrangement for the impedance measurement on a steel macroelement in diluted sulfuric acid.

Fig. 2. A typical mortar specimen with embedded graphite electrodes and steel rebar. The distance between the graphite electrodes was 2 cm.

After curing, a cathodic protection system was applied using a conductive primer as an anode[13]. A voltage of 2 V between cathode and anode was used generating a protection current in the range of 20–500 $\mu A/cm^2$ steel surface depending on the content of chloride. The measurements were carried out with a couple of graphite electrodes, one serving as a reference electrode and the other one serving as a counter electrode.

EXPERIMENTAL

Impedance measurements

Impedance measurements were performed on a FFT-based data system consisting of a fast rising potentiostat (IMP 83, Jaissle, BRD), a dual channel FFT-analyzer (TR 9404, Advantest, Japan) and a digital function generator (TR 98202, Advantest, Japan) controlled via GPIB by an IBM compatible PC-AT 486/25. Data manipulation was done using the program SCADA[14]. The FFT-analyzer and function generator were used in single sine sweep mode. This is used to avoid erroneous evaluation of nonlinear response of the system. About 50 sine waves at a peak to peak amplitude of 10 mV in the frequency range from 25 mHz to 1 kHz were applied in each run for the measurements on steel in concrete (for steel in sulfuric acid the frequency range was from 25 mHz to 200 Hz).

Each data set consists of the following values: time relative to the start of the experiment, applied frequency, real and imaginary component of system impedance.

Linear polarization resistance measurements

The measurements were controlled by an IBM compatible PC-AT-386/33 with a specially designed 12 bit A/D interface (Burr Brown ADC 80). A STV function generator (12 bit/ $\pm$ 2.5 V) connected via RS 232 was used via the software package CSTATIE[15]. Five cyclic voltage scans in the range of $\pm$ 10 mV around the rest potential with 1.22 mV/ 1.22 s steps were applied for each experiment.

RESULTS AND DISCUSSION

Steel bar in sulfuric acid

Figure 3 shows impedance spectra for the steel macroelement in 0.1 N sulfuric acid. The impedance plot for the active area is depicted on the left side, for
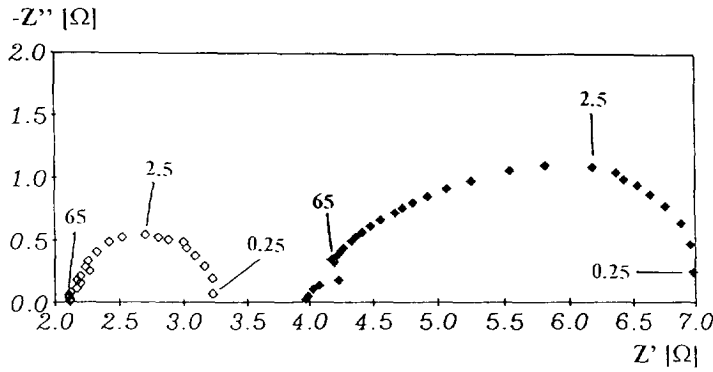
Fig. 3. Impedance spectra measured at the steel macroelement in 0.1 N sulfuric acid. Left side: active area; right side: passive area; frequency range: 250 mHz to 200 Hz, amplitude 10 mV p-p.
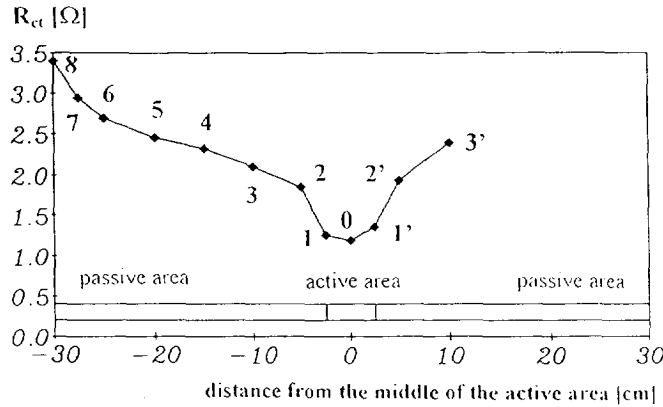

Fig. 4. Calculated R_{ct} values with increasing distance of the middle of the active area (mild steel); measuring parameters as in Fig. 3.

the passive area on the right side. The so called R_{ct} values (indicating the corrosion current densities) for the corrosion reactions are evaluated using the same model as Wenger and Galland[12]. Figure 4 depicts the evaluated R_{ct} values, increasing with the distance from the active area. In a further step, these R_{ct} values were used to develop a simple measuring technique for the application in real systems.

Since for the system "steel in concrete" the imaginary arc of the impedance at low frequencies (2.5 mHz) still is very high ($\tau \approx 1000$ s[16]), it is difficult to evaluate the R_{ct} values with the same procedure as discussed just before. As for the controlling of the effectiveness of a CP system only *changes* in the R_{ct} values are relevant, the measurement of absolute values is not necessary. So we try to evaluate R_{ct} values by a "two frequency method".
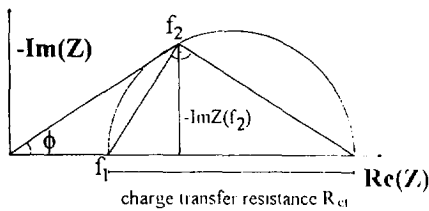
For the calculation of R_{ct} values based on measurements at two frequencies an ideal Randels-circuit was assumed (capacitance with $\phi = -90°$). In this case an estimation of the R_{ct} in the Nyquist diagram *via* Thales circle should be possible. For this purpose only the knowledge of the impedance values measured with one high frequency (R_Ω) and with one frequency in the medium range is necessary (Fig. 5).

In most cases the real Nyquist impedance plots are depressed semicircles and therefore the use of this method will deliver smaller values for the R_{ct} as the correct ones (Fig. 6). These values calculated
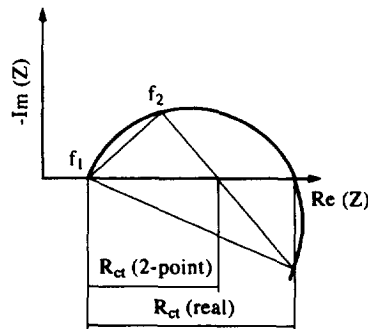

Fig. 5. Estimation of the R_{ct} values *via* the Thales circle in the case of measuring the impedance with two frequencies.

Fig. 6. Extrapolation of the R_{ct} values measured at two frequencies in the case of a depressed semicircle (extrapolation to a "too small R_{ct} value").
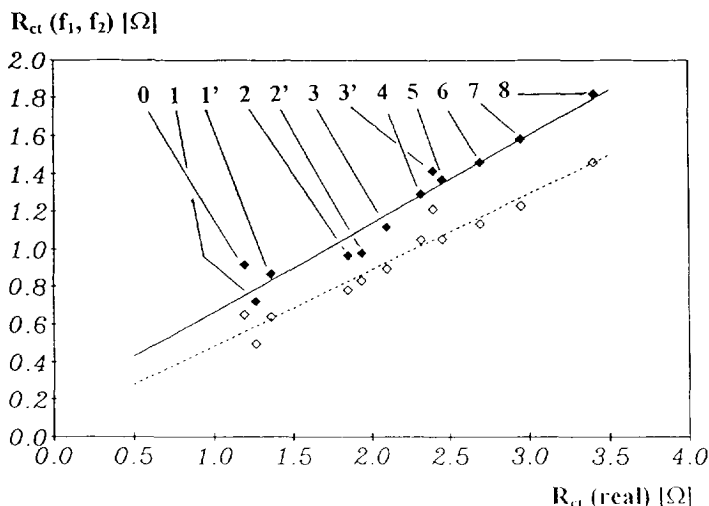
Fig. 7. Correlation between the R_{ct} values measured in the frequency range 250 mHz to 200 Hz (R_{ct}(real)) and the R_{ct} values obtained by using two selected frequencies and extrapolating via Thales circle ($R_{ct}(f_1, f_2)$). Data from measurements on a steel macroelement in 0.1 N sulfuric acid; the numbers refer to the numbers in Fig. 4: ◇ measured at 20 and 200 Hz; ◆ measured at 10 and 200 Hz.

from two frequencies correlate linearly with the the wide frequency range measured R_{ct} values (Fig. 7). This figure shows R_{ct} values calculated from measurements at two frequencies (200 Hz and 10 Hz, 200 Hz and 20 Hz) in relation to the R_{ct} data determined by measuring in the frequency range of 250 mHz to 200 Hz. These frequencies were chosen based on the similarity of the Nyquist diagrams measured on steel in sulfuric acid and on steel in concrete, respectively. Performing the calculations with four or six frequencies delivers the same results. The different measuring points are the same as in Fig. 4, (dependence on the distance of the active area of the steel macro-element).

Linear regression of the R_{ct} values for 200 and 10 Hz values and the real R_{ct}'s leads to the equation:

$$R_{ct}(200\,Hz, 10\,Hz) = 0.470 \times R_{ct}(real) + 0.194\ [\Omega]$$

$$(r = 0.96).$$

For the frequencies 200 and 20 Hz the relation is:

$$R_{ct}(200\,Hz, 20\,Hz) = 0.239 \times R_{ct}(real) + 0.074\ [\Omega]$$

$$(r = 0.96).$$

Steel bar in mortar

The impedance measurements on steel bars in the mortar samples were carried out using one graphite electrode as a reference electrode, the other one has a counter electrode and the steel bar as the working electrode (frequency range: 250 mHz to 1 kHz). Figure 8 shows typical impedance diagrams for steel in concrete samples without chloride ions and with 2% chloride ions. Steel in the sample without chloride exhibits a higher R_{ct} value in comparison to the sample with a chloride content of 2%. The spectra were measured after 28 days of curing time. For the observation of a change in the rebar with ongoing CP, the CP current was switched off and the impedance measurements were carried out after a complete

depolarization of the rebar. Usually, this depolarization needs a time of approximately 24 h.

To visualize the change of the corrosion situation of the steel bars in the different concrete samples, the relative corrosion rates were calculated and were settled for each sample before application of the CP to a value of one. The relative corrosion rates are the reciprocal values of R_{ct} in relation to the initial values (the value for the sample without chloride after curing without CP was set to one).

No change of the relative corrosion rate was observable for the steel bar in the mortar sample without chloride where the steel rebar is passive. Figure 9 shows the change of the relative corrosion rates for the sample without and with 1% and 2% chloride. There is a clear change in the corrosion rates of the steel bars in the mortar samples with 1% and 2% chloride with ongoing CP; the relative corrosion rates were reduced by a factor of about 0.5
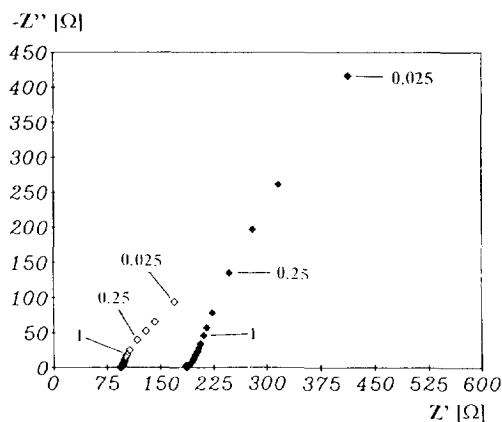

Fig. 8. Typical impedance diagrams for steel in concrete; frequency range: 25 mHz to 1000 Hz; 10 mV pp: ◇ sample with a content of 2% chloride in concrete; ◆ sample without chloride.
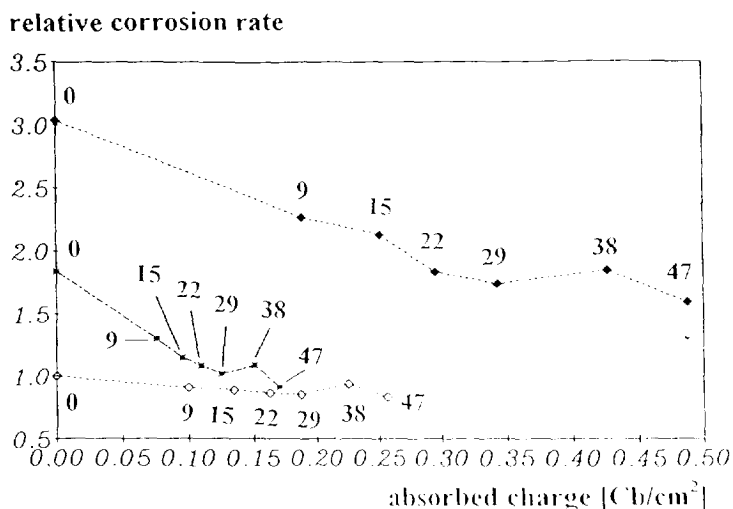
relative corrosion rate

Fig. 9. The change of the relative corrosion rates for three samples with continuous CP in dependence on the charge consumed. Measuring conditions: 250 mHz and 1000 Hz, 10 mV p-p; numbers indicate the days of applied CP (voltage of 2 V): ◇ without chloride in concrete; * 1% chloride in concrete; ◆ 2% chloride in concrete.

after 47 days. To verify the "2-frequency-measurement" of R_{ct} of steel in concrete, additionally LPR measurements on the same electrodes under identical conditions were performed. Figure 10 shows the LPR measurement for the samples without and with 2% chloride after the 28-day curing. The different slopes of both curves are clearly distinguishable. The calculations of the polarization resistance (R_p) were done according to[17]. The values for the electrolyte (mortar) resistance (R_Ω) measured at a frequency of 1 kHz were subtracted from all R_p values. All collected data were used to correlate the "2-point charge transfer resistance" with the corrected R_p values. For the overall correlation the mean values of four measurements (four pairs of graphite electrodes) were used.

A good linear correlation was observed for the values determined using the two different methods as

depicted in Fig. 11. The enhancement of the R_{ct} with charge consumed during CP applied is evident, too. The R_{ct} values for the samples without chlorides show a larger variation, but no real change with the charge consumed during CP.

CONCLUSIONS

Using EIS at two frequencies and calculating the R_{ct} values, information concerning the corrosion situation of steel rebars in concrete could be obtained.

The changes in the corrosion rates of steel in different Cl⁻ contaminated concrete specimens with applied CP were also detectable. The transfer resistance for the corrosion reactions of active steel in concrete increases with the charge used during the
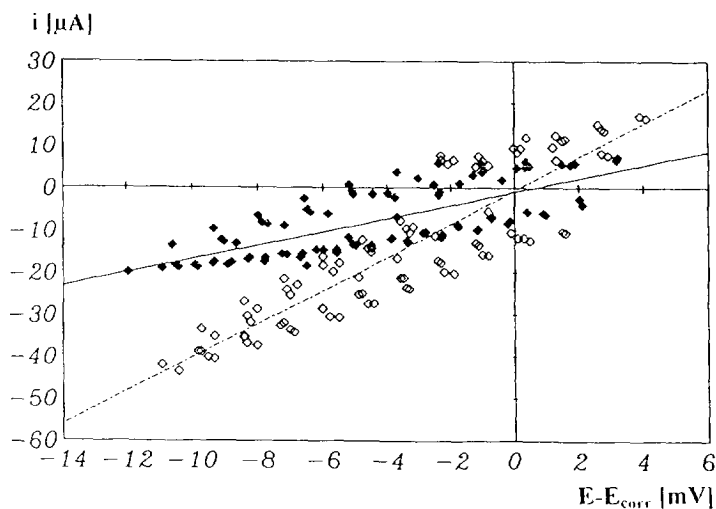

Fig. 10. Linear polarization measurements on the samples without chloride (◆) and with 2% chloride (◇) in the concrete after 28-day curing. Measuring conditions: pulse height 1.22 mV, duration 1.22 s.
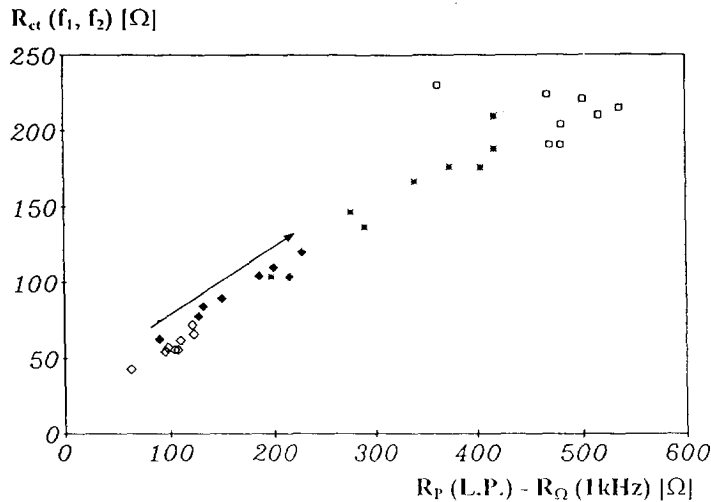
Fig. 11. Correlation for the R_{ct} values measured with the "2-frequency-methode" (conditions as in Fig. 9) and linear polarization technique (conditions as in Fig. 10). The arrow indicates the direction of changes in the charge transfer resistance with cathodic protection: □ sample without chloride; * sample with 1% chloride; ◆ sample with 2% chloride; ◇ sample with 3% chloride.

CP treatment. No change in the corrosion rates of passive steel with the charge absorbed during CP was measured and therefore measurements on passive areas could be used as a reference. The increase of the transfer resistance can be explained by the repulsion of the chloride ions from the rebar surface and with the increase of alkalinity caused by the cathodic reaction (oxygen reduction).

The measurement technique developed during this work allows the characterization of a large number of corroding areas in a fast and efficient way and can be used for the monitoring of the effectiveness of cathodic protection systems also in large installations.

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