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THE CORROSION KINETICS AND MECHANISM OF HOT DIP GALVANIZED REBARS IN ADDITIVATED CONCRETE

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Abstract: *The reinforced concrete is one of the most frequently used composite materials. The corrosion of the rebar is one of the most important factors that have an influence on the life and exploitation costs of reinforced concrete structures. Hot dip galvanizing the rebar is an efficient but still controversial corrosion protection method. The paper presents the researches regarding the corrosion resistance of hot dip galvanized compared to unprotected rebars. The corrosion resistance was studied by electrochemical techniques (chronoamperometry, linear polarization and electrochemical impedance spectroscopy EIS). Also, the influence of cement type and additive used to prepare the concrete on the kinetic parameters and mechanism of the phenomenon are presented. The experimental results showed that the corrosion resistance is higher for hot dip galvanized rebars than for unprotected ones.*
Key words: *hot dip galvanized rebar, corrosion, chronoamperometry, linear polarization, EIS*

1. INTRODUCTION.

The rebar corrosion is one of the most important factors that determine the life of one of the most frequently used composite materials, reinforced concrete. According to the literature data [2, 9], the use of hot dip galvanized rebars leads to a significant increase of the life of reinforced concrete components. This is due to the Zn / Zn-Fe alloy coating formed and metallurgicaly bonded to the steel substrate that actions by a mechanism that combines barrier effect with cathodic protection.

The use of high resistance concretes, compacting concretes, special concretes represents a real interest in the civil and industrial construction field. The production of more and more compact concretes, with increased workability and high resistance to mechanical stress, as currently required, is possible only by introducing additives. Currently there are few studies on the corrosion behavior of hot dip galvanized rebar in additivated concrete. The presented paper opens new study opportunities, especially regarding the behavior of hot dip galvanized rebar in concrete with additives content that have complementary or different influences.

The experimental work presented in the paper studied the individual influence of two additives, frequently encountered in concrete production: Addiment Verzigerer VZ 1, superplasticizer, phosphate based hardening delayer, respectively Sika Viscocrete – 1040, universal superfluidizer with a strong effect for transport concrete. Also, the influence of the type of cement used for the preparation of the concrete on the corrosion of the rebar was studied. Two types of cement were used: Portland cement CEM I 42,5 N and composite Portland cement CEM II/B-M 42,5 N.

The original scientific character of the paper is given by the use of modern and current techniques in studying the kinetics and mechanism of the corrosion process of the rebar in concrete that assured clear and easy to interpret results, similar with the data from the literature [1-9].

2. EXPERIMENTAL RESULTS

For the experiments, prismatic concrete samples were made and PC 52 ø 8 mm rebars were introduced verticaly and centered. Some of the samples were introduced in the concrete without any corrosion protection pre-treatments, unprotected (N). Other stell bars were hot dip galvanized in a molten zinc bath at 450°C before beeing introduced in the concrete. The thickness of the zinc coating was determined by the destructive method, chemically as well as by magnetic method and was 140 µm [11, 12].

The concrete was prepared according to NE 012-2007 – Code of good practice for the execution of concrete, reinforced concrete and precompressed concrete works, so that it would correspond to a C 20/25 concrete class, with a water / cement ratio of 0,4. Portland CEM I 42,5 N and composite Portland cement CEM II/B-M 42,5 N were used. To additivate the concrete a quantity of additive of 1% from the cement quantity was used.

The reinforced concrete samples were kept in laboratory conditions until reaching 28 days since casting and were coded as follows: type of steel (unprotected N / hot dip galvanized ZT) – type of cement used to prepare the concrete (Portland cement I / composite Portland cement II) – type of additive used to prepare the concrete (without additive witness / with additive Addiment Verzigerer VZ 1 / with additive Sika Viscocrete 1040).

The electrochemical tests and the recording of the experimental data were made on a VOLTALAB 10 potentiostat connected to a computer. The electrochemical cell used was composed of: electrolyte – NaCl 3% solution, $Ag/AgCl_2$ reference electrode and platinum counter electrode, the work electrode beeing the steel bar embedded in the concrete itself.

The Electrochemical Impedance Spectroscopy (EIS) measurements were realized at 23°C, in an alternative current range of f = 100kHz - 100 mHz and amplitude of 10 mV, at the open circuit potential value. The Nyquist (the imaginary component of the impedance as a function of the real component) and Bode diagrams (logarithmic representations for the impedance-frequency modulus and phase-frequency angle) were raised.

The equivalent electric circuit on which the mathematical modeling of the phenomenon was based and that generated the best fitting of the EIS diagrams is presented in figure 1. The rebar's corrosion in concrete kinetic parameters and mechanism were determined by fitting the Nyquist and Bode diagrams with the help of this equivalent electric circuit.

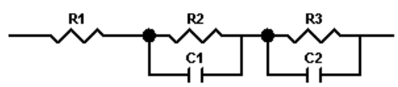


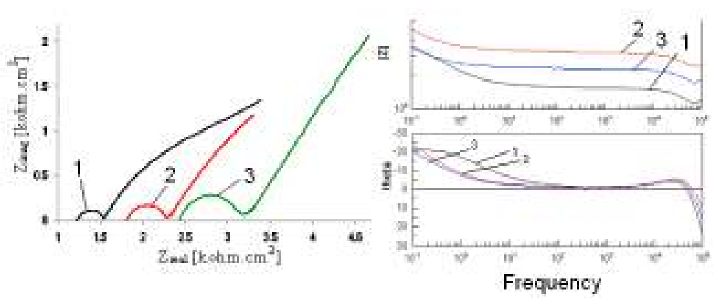
Figure 1. The equivalent electric circuit used for fitting the EIS diagrams

The experimentally obtained diagrams are presented in figures 2 and 3 for concrete prepared with Portland cement with hot dip galvanized or unprotected rebars. For concrete prepared with composite Portland cement, the obtained diagrams are similar.

Based on these measurements the following conclusions can be drawn regarding the influence of the additives on the rebar's corrosion mechanism:

- The increase of the diameter of capacitive loops (see Nyquist diagram) with the activation of the concrete means the reduction of the corrosion process in that direction. The increase sign of corrosion resistance is the increase of the polarization resistance. This happens differently, depending on the type of additive that was used. Thus, it was observed that Addiment Verzigerer additive has a bigger influence on the corrosion mechanism of the rebar in concrete than Sika Viscocrete. Also, the higher polarization resistance values obtained for hot dip galvanized compared to the unprotected steel means an increase of the corrosion resistance as a result of hot dip galvanizing the rebar.

- The parallelism of the Bode diagrams obtained for the same type of steel, in concrete prepared with the same type of cement, but with or without additive content, shows that adding additives to the concrete doesn't influence the corrosion's process mechanism, only the parameters at which it appears.

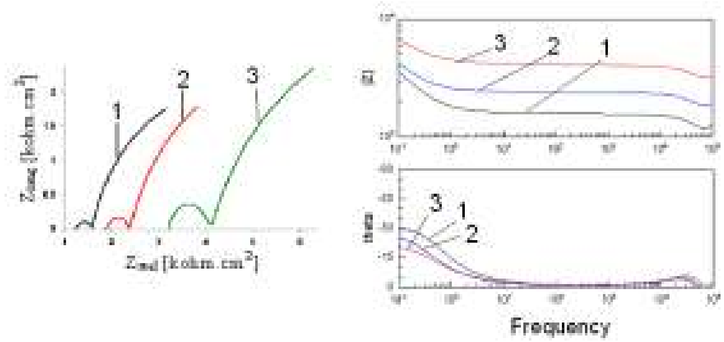


Legend: 1 – ZT I witness; 2 – ZT I Sika Viscocrete 1040; 3 – ZT I Addiment Verzigerer VZ 1

Figure 2. Nyquist and Bode diagrams for concrete samples prepared with Portland cement and hot dip galvanized rebar

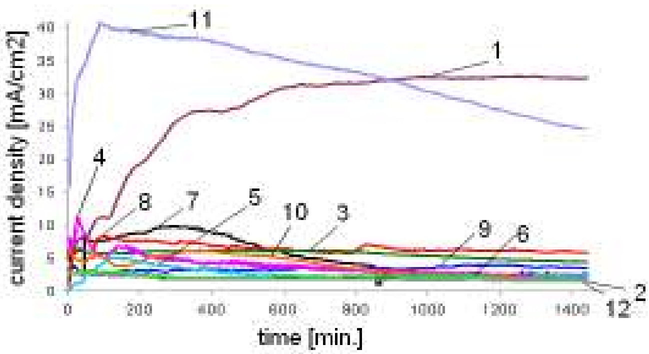
The kinetic of the corrosion process of the rebar in concrete was studied using the chronoamperometry and linear polarization methods.

By applying a constant potential of 500±5 mV, the current density evolution curves as a function of time were recorded on a 24 hours period (figure 4. – 6.). Because the current density is a measure of the corrosion rate, the corrosion rate of the hot dip galvanized steel versus the one of the unprotected steel can be comparatively evaluated, related to the concrete composition (with or without additive, type of additive and type of cement).



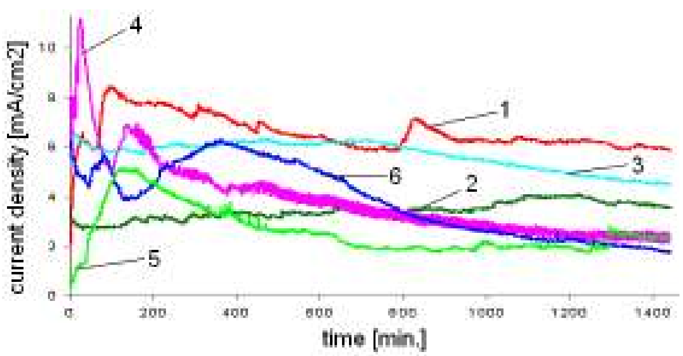
Legend: 1 – N I witness; 2 – N I Sika Viscocrete 1040; 3 – N I Addiment Verzigerer VZ 1

Figure 3. Nyquist and Bode diagrams for concrete samples prepared with Portland cement and unprotected rebar



Legend: 1 – N II witness; 2 – N II Sika Viscocrete; 3 – N I Addiment Verzigerer; 4 – ZT I witness; 5 – ZT I Sika Viscocrete; 6 – ZT II Addiment Verzigerer; 7 – N II Addiment Verzigerer; 8 – N I witness; 9 – N I Sika Viscocrete; 10 – ZT I Addiment Verzigerer; 11 – ZT II witness; 12 – ZT II Sika Viscocrete

Figure 4. Current density, in time, for samples with unprotected and hot dip galvanized rebars in concrete prepared with Portland cement and composite Portland cement, with Addiment Verzigerer VZ 1 and Sika Viscocrete 1040 additives

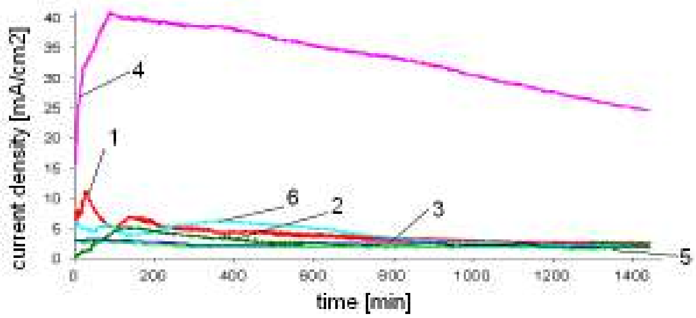


Legend: 1 – N I witness; 2 – N I Sika Viscocrete; 3 – N I Addiment Verzigerer 4 – ZT I witness; 5 – ZT I Sika Viscocrete; 6 – ZT I Addiment Verzigerer

Figure 5. Current density representation as a function of time for unprotected and hot dip galvanized steel embedded in concrete prepared with Portland cement with additives

According to figures 4.-6.:

- Hot dip galvanized steel (ZT) presents lower current density values than the unprotected steel (N). In the same type of concrete the
- The cement also has a significant influence on the rebar's corrosion behavior because of its oxidic composition. Thus, preparing the concrete without additives and using composite Portland cement generates higher current density values for the samples with unprotected (N) or with hot dip galvanized steel (ZT). It was though observed that the additivation of the concrete prepared with Portland cement does not determine so important decreases of the current density as for when concrete prepared with composite Portland cement was additivated.
- Using additives to prepare the concrete determines for both the types of cement used a decrease of the current density, for the samples with unprotected rebars (N) as well as for the ones with hot dip galvanized rebars (ZT). This can be accepted and explained because of the influence that the additive has on the structure of the concrete. In the studied cases the additivation determines a decreased permeability of the hardened concrete to liquids and aggressive gases.
- The use of Sika Viscocrete 1040 additive determines a higher decrease of the current's density than by using the additive Addiment Verzigerer VZ.
- The descending trend of the recorded curves for all the types of concrete that had hot dip galvanized rebars must be noted. Although initially in the first 90 minutes of the experiment, the current density for the concrete sample with composite Portland cement, without additives and with hot dip galvanized rebar had a strongly ascendant trend, after this, the descendant slope is similarly steep. So, in this case, the corrosion rate not only reduces but becomes lower than the corrosion rate of the similar sample but with unprotected steel rebar.



Legend: 1 – ZT I witness; 2 – ZT I Sika Viscocrete; 3 – ZT I Addiment Verzigerer; 4 – ZT II witness; 5 – ZT II Sika Viscocrete; 6 – ZT II Addiment Verzigerer

Figure 6. Current density evolution in time, for samples with **hot dip galvanized rebars** embedded in concrete prepared with Portland cement or composite Portland cement and additives

The linear polarization curves were raised in continuous current, by sweeping the potential applied to the work electrode in the domain ±300 mV from the open circuit potential value (figure 8 – 9). Based on them, the kinetic parameters of the phenomenon, the corrosion potential as well as the corrosion current and rate were determined (figure 7).

The efficiency of the protection conferred by hot dip galvanizing the rebar was calculated for each type of concrete with fomula 1. The results are presented in table 1.

$$P = \frac{v_{cor}^{N} - v_{cor}^{ZT}}{v_{cor}^{N}} * 100\,[\%] \qquad (1.)$$

where: v_{cor}^{N} = the corrosion rate of the unprotected steel, expressed in μm/year;

v_{cor}^{ZT} = the corrosion rate of hot dip galvanized steel, expressed in μm/year;

Table 1. Corrosion protection efficiency by hot dip galvanizing

Type of cement used to prepare the concrete	Witness concrete (without additives)	Additivated concrete with Addiment Verzigerer VZ 1	Additivated concrete with Sika Viscocrete-1040
Portland cement	0,79	11,27	22,98
Composite Portland cement	21,25	21,19	50,87

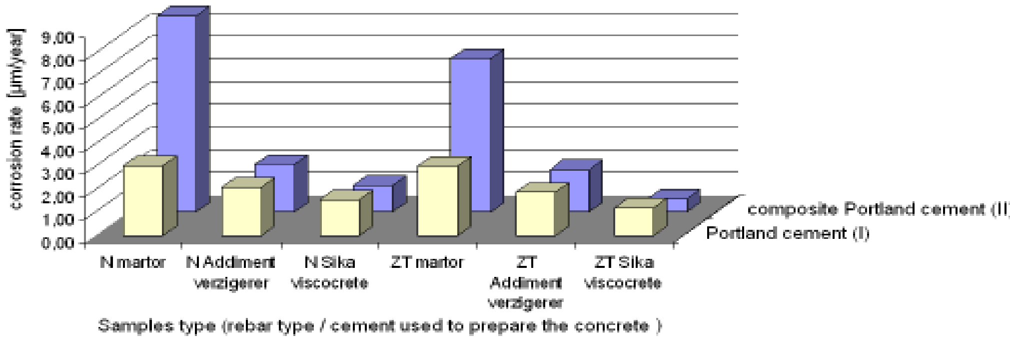
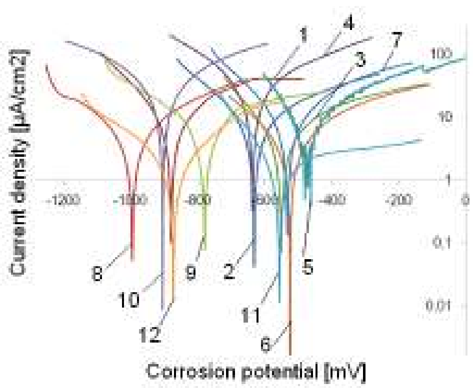


Figure 7. Corrosion rate.

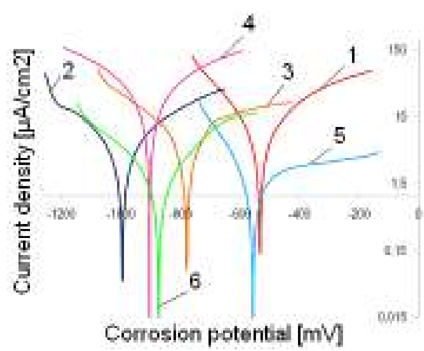
Based on the linear polarization curves and on the determined kinetic parameters, it can be said that:

- At low values of the overpotential, the corrosion process is controlled by the chemical reactions that take place, and at high values of the overpotential a diffusive control also appears, probably because of the formed layer of corrosion products.
- The corrosion current, regardless if the rebar is hot dip galvanized or not, decreases with the introduction of additives in the concrete prepared with Portland cement or composite Portland cement. The additive Sika Viscocrete 1040 has a stronger influence of reducing the corrosion current than Addiment Verzigerer VZ 1 additive. Thus, the corrosion rate is reduced by using additives in concrete, differentiated according to the type of additive used.
- The use of composite Portland cement has a positive influence on the corrosion resistance of the rebar, hot dip galvanized or not. The decrease of the corrosion rate is stronger if the additivated concrete is prepared with composite Portland cement. The efficiency of the corrosion protection by hot dip galvanizing is very high if Sika Viscocrete additive is used.
- Depending on the type of additive used, the corrosion potential can be shifted in positive or negative direction, thus we can't precisely estimate the probability of corrosion initiation.



Legend: 1 – N I witness; 2 – N I Addiment Verzigerer; 3 – N I Sika Viscocrete; 4 – N II witness; 5 – N II Addiment Verzigerer; 6 – N II Sika Viscocrete; 7 – ZT I witness; 8 – ZT I Addiment Verzigerer; 9 – ZT I Sika Viscocrete; 10 – ZT II witness; 11 – ZT II Addiment Verzigerer; 12 – ZT II Sika Viscocrete

Figure 8. Linear polarization curves for unprotected rebar, respectively hot dip galvanized, in concrete without additives, additivated with Addiment Verzigerer VZ 1 or with Sika Viscocrete 1040.



Legend: 1 – ZT I witness; 2 – ZT I Addiment Verzigerer;
3 – ZT I Sika Viscocrete; 4 – ZT II witness; 5 – ZT II Addiment Verzigerer; 6 – ZT II Sika Viscocrete

Figure 9. Linear polarization curves for hot dip galvanized rebar, in concrete without additives, additivated with Addiment Verzigerer VZ 1 or with Sika Viscocrete 1040.

After the visual observation of the tested samples, both in exterior as well as in interior, at rebar – concrete interface, it can be said that:

- On the surface of the concrete that embeds the unprotected steel rust stains appeared. Also, during testing these samples, the color of the electrolyte changes to yellow, a sign of the migration of iron oxides from the surface of the rebar, through the concrete, into the electrolyte. The color is stronger for the samples without additives in the concrete, sign of the formation of a bigger quantity of corrosion products and of an increased porosity of the concrete which favors their easier migration towards the surface of the sample.

- The samples with hot dip galvanized rebar presented no sign of steel corrosion (red rust) at rebar level nor red rust stains on the surface.

3. CONCLUSIONS

Based on the experimental results it can be said that:

- Using Hot dip galvanized rebar to reinforce the concrete gives a good corrosion protection. This effect is also observed for concrete without additives but especially in the case of concrete prepared with additives.
- At a constant potential that was applied, the samples with hot dip galvanized rebar present a lower current density than unprotected ones.
- The kinetics factors, corrosion current and rate are lower for reinforced concrete with hot dip galvanized rebars.
- The corrosion mechanism is not qualitatively influenced by hot dip galvanizing, but quantitatively an increase of the polarization resistance and of corrosion resistance is observed.
- The oxidic composition of the cement used to prepare the concrete influences the kinetic of the corrosion process. Protland composite cement determines an increase of the corrosion protection conferred by hot dip galvanizing. This increase of protection efficiency by hot dip galvanizing is even higher if the concrete contains additives.
- The additive type influences the kinetic of the corrosion process. In the studied cases the influence of additives is especially observed by the impermeability grade of the concrete to gas and aggressive liquids. It is remarkable the higher influence of Sika Viscocrete 1040 additive, especially when used to additivate concrete prepared with composite Portland cement.

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