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KINETICS OF THE CORROSION PROCESS OF HOT DIP GALVANIZED STEEL REINFOCEMENT IN FRESH CONCRETE

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ABSTRACT. The quality of concrete structures is largely reflected by its durability. According to literature, the rebar corrosion initiation is delayed and the life duration of concrete structures reinforced with hot dip galvanized rebar is extended with up to 70 years compared to life duration of concrete structures reinforced with non-galvanized steel rebar. It is well known that the galvanized rebar surface activates in contact with the alkaline environment of fresh concrete, forming a crystalline compound namely calcium hydroxizincate. This crystalline compound is important for the kinetic and corrosion mechanism of rebar embedded in concrete. This work aims to evidence the galvanized rebar corrosion kinetics in fresh concrete, during the concrete hardening. Electrochemical methods were used during experiments. The test results show an activation of the zinc layer of galvanized rebar in contact with the alkaline environment of concrete, during the first days after rebar embedding in concrete. Zinc corrosion products formation lead to better corrosion resistance of galvanized steel rebar, compared to the resistance of non-galvanized steel rebar.

Keywords: *hot dip galvanized steel reinforcement, concrete, corrosion, calcium hydroxizincate*

INTRODUCTION

The quality of reinforced concrete structure is given by its durability, which is the period of time the structure maintains all the characteristics required for the proper use as established in the design. The technical performances of reinforced concrete structures decrease exponentially with time, due to the exponential increase of the degradation rate of both concrete and reinforcement. [1, 2, 8, 9, 15]

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According to literature, the main factors that cause the reinforced concrete degradation are (starting from the most important to the least important): reinforcement corrosion, acid solutions aggression, sulfate attack, alternating wet and dry conditions, repeated freeze-thaw cycles, levigation, internal stress, external forces, salt crystallization, the aggregates reaction with concrete, and abrasion. [10, 11] Note that the reinforcement corrosion is the main cause for concrete degradation and for the reinforced concrete structures and components durability decrease.

Corrosion of reinforced concrete structures should be studied regarding concrete/steel rebar system interaction with the surrounding environment, and regarding the rebar interaction with concrete [12].

Many rebar corrosion protection methods are proposed worldwide, all having both advantages and disadvantages. Among these, hot dip galvanizing of steel reinforcement has been studied for the past 50-60 years and based on theoretical and electrochemical arguments, laboratory and in situ testing, is proved to be one of the most effective corrosion protection methods up to this day. [1-7, 13-16] Hot dip galvanizing is used for 2% of the total amount of steel reinforcement in the US and for 1% in Europe, but these values are increasing every year, especially for the structures designed to be used in extremely corrosive, marine or tropical climate environments. [1, 2, 7, 13-16]

Literature [3-6, 13-16] indicates that corrosion occurs 2-3 days after the hot dip galvanized steel rebar contact with fresh concrete. Corrosion products forms following the corrosion initiation, some of which some play a passivation role, such as calcium hydroxizincate, while other corrosion products, such as zinc oxides and hydroxides - that are insoluble in water, do not have a passivation role. In order to obtain calcium hydroxizincate, about 10 µm thick zinc coating is used. Because the corrosion products layer is adherent and compact at the surface of the galvanized steel reinforcement, it is more resistant to corrosion. On the other hand, zinc is less noble than steel, thus ensuring steel cathodic protection. As such, the steel is protected for as long as the zinc layer is not fully consumed.

Previous results obtained by the authors [17-21] support the fact that by using hot dip galvanized reinforcements the durability of concrete structures is increased and the work in this paper searches to clear the kinetics of the corrosion process of hot dip galvanized steel reinforcement in fresh concrete.

The aim of the experiments was to analyze the kinetics of hot dip galvanized steel rebar in fresh concrete, until concrete hardening. This study is important because most reactions in concrete take place in this phase; such as the cement hydration – hydrolysis, the concrete pH stabilization, and the activation of the hot dip galvanized steel rebar surface, followed by the calcium hydroxizincate formation [13-16].

RESULTS AND DISCUSSION

The experimental chronoamperometry curves were plotted, showing the current density variation for 24 hours, at constant potential. Experimental tests of samples with non-protected or with hot dip galvanized reinforcement embedded in various concrete age were made. Concrete age is given by the time passed since concrete pouring (samples preparations) till the tests. This time, the samples were all kept in identical conditions in laboratory. The results are shown in Figure 1 and Figure 2.

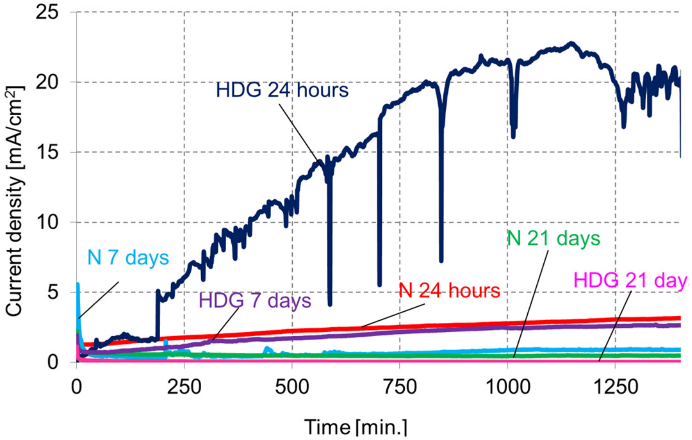

Figure 1. Current density evolution for the galvanized and non-galvanized steel rebar, during concrete hardening

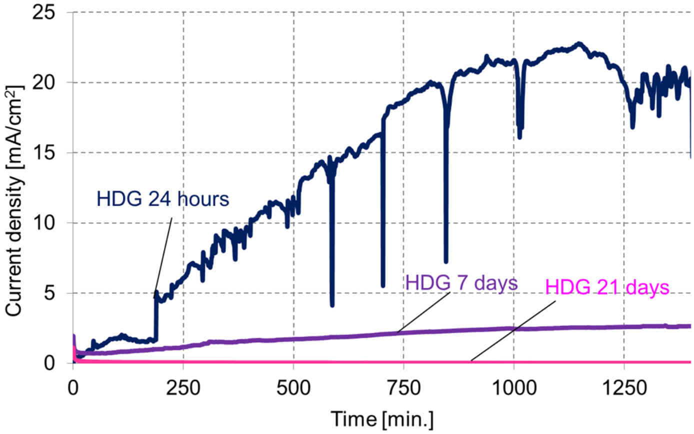

Figure 2. Current density evolution for the galvanized steel rebar in concrete, during concrete hardening

Twenty-four hours after concrete casting, the current density is high in the case of the hot dip galvanized rebar. This was considered an activation indicator due to the fact that the zinc-coating surface of galvanized rebar activates when introduced in alkaline concrete environment. Thus, a fraction of zinc is consumed, resulting specific corrosion products. The peaks of the "HDG 24 hours" plot indicate that the passive layer regenerates. This layer is subsequently attacked by alkaline concrete and destroyed.

According to the chronoamperometry tests of galvanized steel rebar, the corrosion current density strongly decreases after 7, respectively 21 days from the concrete casting (Figure 2). This is a qualitative sign for the zinc corrosion rate dropping due to the formation of a thicker or more compact corrosion products layer. Moreover, as it can be seen, the diagram of concrete/ HDG rebars samples after 21 days since rebars embedment, does not show current densities peaks. This was interpreted as a passive layer formation on HDG rebars surface, enough resistant to prevent metal surface activation and corrosion.

By comparing the data obtained, it can be seen that 24 hours after concrete casting, the zinc coating on steel rebar exhibit a much stronger activation than the non-galvanized steel. The tests conducted 7 days after concrete casting, show that the difference between the current densities of galvanized and non-galvanized reinforcement is much lower compared to the values found 24 hours after rebar embedding in concrete. However, the values obtained for the galvanized steel samples are higher, showing a higher corrosion rate compared to that of the non-galvanized steel rebar.

Twenty-one days after rebar embedment in concrete, the current density drops significantly, both for the galvanized and non-galvanized rebar. This was considered a stabilization point for the two metals surfaces due to the formation of specific corrosion products layer. This time however, the current density of galvanized steel was very low; it almost linearly increased with time and was lower than the current density of non-galvanized steel.

Twenty-one hours after rebar embedment in concrete, the galvanized steel showed a lower corrosion rate compared to the non-galvanized steel, due to the protective corrosion products layer formation on zinc surface. Although this corrosion products passive layer also formed on the non-galvanized steel surface, the passivizing capacity of the corrosion products layer on zinc surface was stronger, as shown by the current density decrease with time.

The linear polarization plots recorded, in Tafel interpretation, are shown in Figure 3. The corrosion potential, corrosion current and corrosion rate are shown in Table 1.

From Figure 3 and Table 1 it can be seen that the galvanized rebar/ fresh concrete system, noted with „initial HDG", show the more negative corrosion potential (-1424 mV). This indicates a powerful activation of the zinc surface immediately after rebar embedment in the alkaline environment of fresh concrete. Also, the corrosion current of this system is the highest (115.62 μA/cm^2), indicating a high corrosion rate. On contrary, the non-galvanized steel rebar/ fresh concrete system, noted with „initial N", shows a potential shifts toward positive values, with 794 mV, but still remaining in the negative domain of metal surface activation. The corrosion current recorded for the non-galvanized rebar system is lower compared to the galvanized rebar system. Thus, the corrosion rate of the non-galvanized steel rebar system is lower immediately after rebar embedment in fresh concrete, when compared to the galvanized rebar system.

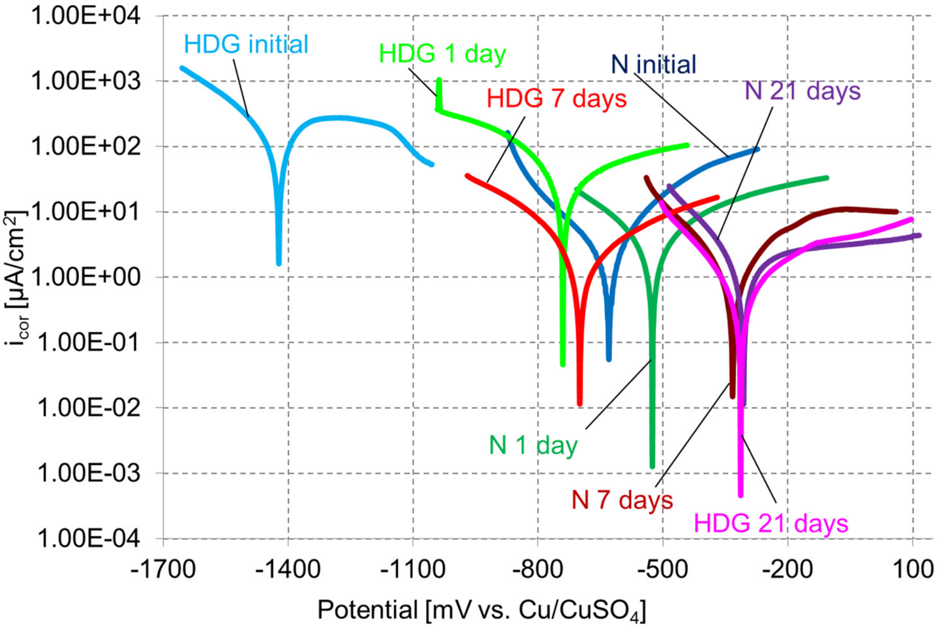

Figure 3. Tafel plots recorded for the samples with galvanized or non-galvanized steel rebar in concrete

Tests conducted 24 hours after rebar embedment in concrete show a corrosion potential fast shifting toward positive values and a corrosion current decrease, for all samples. Even so, the corrosion potential of galvanized steel remains more negative, with 215 mV, and the corrosion current values remains much higher compared to the non-galvanized steel. These results are also supported by literature. According to literature [3-6], zinc reacts with the alkaline environment when introduced in fresh concrete, forming a passive layer that is essential for subsequent corrosion protection.

The electrochemical systems kept in laboratory for 7 days were tested. The results showed passivation of both rebar types, as the corrosion potential shifted towards positive values. Also, the corrosion current decreased.

Between day 7 and day 21, the both rebar system starts to stabilize. The corrosion potential becomes more positive and the corrosion current values decrease. During this period of time, the differences between the two rebar systems corrosion potentials and corrosion currents are smaller compared to previous time intervals.

Table 1. Kinetic corrosion parameters determined from the polarization curves for the galvanized and non-galvanized steel samples, at various concrete ages

Electrochemical system	E [mV]	$i_{cor.}$ [μA/cm^2]	$v_{cor.}$ [μm/an]
N Initial	-630	19.59	227.19
N 1 day	-525.5	12.11	140.48
N 7 days	-333	1.18	13.69
N 21 days	-313.5	0.94	10.94
HDG initial	-1424	115.62	1734.37
HDG 1 day	-740.5	60.80	911.97
HDG 7 days	-701.5	1.62	24.36
HDG 21 days	-315	0.65	9.69

Tests conducted on the electrochemical systems 21 days after concrete casting indicate rebar passivation. The corrosion potential for the galvanized steel sample is -315 mV, and for the non-galvanized steel sample is -313.5 mV. Also, the corrosion current strongly decreases in both rebar types.

As seen in Figure 3, the corrosion current of galvanized rebar is lower 24 hours after concrete casting. During the first 7 days after rebar embedding in concrete, the potential shift toward positive values is stronger (with 722.5 mV). In the same time, the corrosion current decreases. According to this data, most of the passive layer forms during this period of time. Experimental results show that the passive layer does not form during the first 24 hours from the rebar embedding in concrete. During the time interval between day 7 and day 21, the corrosion current decrease was lower (0.98 μA/cm^2), even though the corrosion potential shifted significantly toward positive values (386.5 mV).

The changes that occur in the corrosion kinetics of the non-galvanized steel, as shown in Figure 3, are not as significant when compared to the galvanized steel system. The corrosion potential shifts toward positive values, indicating the steel passivation in hardened concrete. The corrosion current also decreases. Although the non-galvanized steel system corrosion current is initially lower compared to the galvanized steel, 21 days later after rebar embedment in concrete, it becomes higher. This shows a higher rate of non-galvanized steel corrosion, 21 days after concrete casting.

Regarding the effectiveness of corrosion protection, the galvanized rebar showed a higher corrosion rate in the first 7 days when compared to the non-galvanized rebar. During the time interval between day 7 and day 21 from rebar embedment in concrete, the corrosion rates of both rebar types reverses. The effectiveness of corrosion protection EP (Scheme 1) becomes positive: 11.45%. This is an indicator of a passive layer formation on the galvanized rebar surface.

If we consider the corrosion rate constant during the first 7 days after rebar embedment in concrete and equal with the initial corrosion rate, the zinc layer thickness would decrease with approximately 34 µm. If we consider the corrosion rate constant during the first 7 days after rebar embedment in concrete and equal to the corrosion rate in the 7th day after rebar embedment in concrete, a 0.5 µm zinc layer thickness would have been consumed. As the corrosion rate is not constant during this time interval, the simple arithmetic mean of these two values was calculated. Thus, the consumed zinc layer calculated thickness, of approximately 17 µm, is close to the values found in the literature (10-15 µm) when an efficient passive layer forms on the galvanized rebar surface.

According to data shown in Table 1, neither of the rebar systems reaches the passive state condition 21 days after concrete casting. According to Table 1, the corrosion potential of the HDG electrochemical system, 21 days after concrete casting (HDG 21), indicates a lower rebar corrosion, close to passivation state, while the corrosion potential of the N 21 system, indicates a higher rebar corrosion (50%).

CONCLUSIONS

The conclusions from experimental data are:

1. Zinc surface activates after galvanized steel rebar embedment in fresh concrete. This is evidenced by the corrosion current density recorded using chronoamperometric method and by the kinetic parameters recorded using the linear polarization method. All the experimental values found decreased with time (hours, days) after galvanized rebar embedding in fresh concrete.

2. The studied parameters decrease with time was due to a passive layer formation on the galvanized rebar surface, which inhibits corrosion process. Additional testing of passive layer was not conducted, considering it was as described/ in accordance with literature.

3. The galvanized steel rebar surface showed an initial higher activation compared to the non-galvanized steel rebar. However, it displayed a faster and stronger passivity. Thus, the corrosion potential shift toward positive values was more significant (1109 mV) for the galvanized sample, compared to the non-galvanized sample corrosion potential (316.5 mV). Also, the galvanized steel rebar corrosion rate decreased in time from higher values (911.9 μm/year) compared to the non-galvanized steel rebar corrosion rate (of 227.2 μm/year) to lower values (9.7 μm/year) compared to the non-galvanized rebar (10.9 μm/year).

Initially, the HDG steel surface strongly activates due to contact with alkaline concrete. Corrosion products form on the galvanized surface, with passivation role, as shown by the corrosion potential shifting toward positive values and by the corrosion current and corrosion rate values decrease. Twenty-one days after both reinforcement types embedment, the kinetic parameters show a much more reduced corrosion of HDG rebars corrosion compared to non-galvanized rebars.

EXPERIMENTAL SECTION

The electrochemical cell used, as shown in Figure 4, has the following components: the working electrode (the rebar), the reference electrode - $Cu/CuSO_4$, and the graphite counter electrode, all embedded in the fresh concrete matrix. All the experiments were conducted on the same concrete type; using PC 52 ø8 mm reinforcement, and using hot dip galvanized (HDG) or non-galvanized (N) rebar samples.

The reinforcement rods were galvanized by immersion in a hot galvanizing bath at a temperature of 450°C, thus obtaining a 140 μm thick zinc layer. The coating thickness obtained through hot dip galvanizing was determined by electromagnetic method, using a PHYNIX – Surfix device, and by testing the coating dissolution, according to SR ISO 1460 and SR EN ISO 2178.

The samples were built by introducing the three electrodes (working electrode, reference electrode and counter electrode) in fresh concrete (right after concrete preparation). The samples were kept in laboratory conditions until testing.

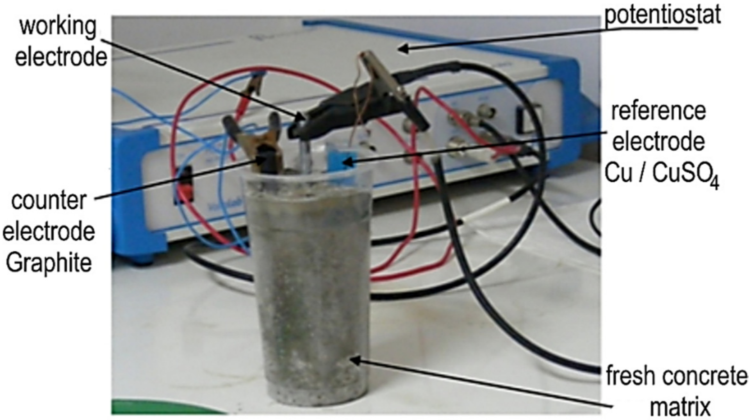

Figure 4. The electrochemical cell

The C 20/25 class concrete was prepared according to the mix design shown in Table 2, according to NE 012-2007 normative. The CEM I 42.5N cement used had the oxide composition as shown in Table 3.

The built electrochemical systems were coded as following:

(HDG x) – Hot dip galvanized steel rebar in concrete; tested x days after rebar embedment in concrete;

(N x) – Non-galvanized steel rebar in concrete, tested x days after rebar embedment in concrete.

Table 2. The concrete used for samples building, submitted to electrochemical testing

The basic components for 1 m^3 concrete		[Kg/ m^3 concrete]
Water		123
CEM I 42.5N cement		308,3
Total of aggregates		1869
Size of aggregates used [mm]	0-4 mm	1121,4
	4-8 mm	747,6

Table 3. The oxide composition of the cement used for the concrete preparation

No.	Cement type	Oxide composition [%]										
		P.C.	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	SO_3	Cl^-
1	CEM I 42.5 N	2.05	15.06	6.23	3.5	61.9	7.0	1.0	0.25	0.31	2.58	0.015

Information regarding the process kinetics is obtained by analyzing the chronoamperometry curves at the constant potential of 500 mV (vs. Cu/CuSO4). The current density was recorded every 60 seconds for 24 hours at various concrete maturation stages (1 day, 7 days, 21 days after rebar embedment in concrete).

Quantitative information was obtained using linear polarization. The potential scanned with a rate of 2 mV/sec, for ±300 mV compared to the open circuit potential, at room temperature. Based on the Tafel experimental plots, the main kinetic indicators were recorded (corrosion potential, corrosion current and corrosion rate). The experiments were conducted after various numbers of days since rebar embedment in concrete (immediately after, and 1, 7 and 21 days after rebar embedment in concrete).

The effectiveness of corrosion protection offered by hot dip galvanization method for each time period after the concrete preparation was calculated using equation (1)

$$\mathrm{EP} = \frac{v_{cor.}^{N} - v_{cor.}^{ZT}}{v_{cor.}^{N}} * 100[\%] \tag{1}$$

where:
$v_{cor.}^{N}$ = non-galvanized steel corrosion rate, [mm/year];
$v_{cor.}^{ZT}$ = galvanized steel corrosion rate, [mm/year].

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