MIGRATING ORGANIC CORROSION INHIBITORS FOR PROTECTION OF STEEL REINFORCEMENT

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Abstract

Steel reinforcement of concrete structures is normally passivated due to high pH value of concrete interstitial electrolyte (pH 13-14). However, chloride contamination (e.g. deicing application, marine environment) can initiate a local breakdown of passive layer and corrosion of rebar. One of the most effective methods to stop or reduce the chloride-induced corrosion of rebar is the use of corrosion inhibitors. As corrosion inhibitors are widely used inorganic nitrites as preventive corrosion inhibitors or organic compounds of different composition (e.g. based on amines and alkanolamines) as curative corrosion inhibitors. The paper is focused on applicability of commercial products based on dimethyldidecyl ammonium (bi)carbonate and polyethyleneimine as corrosion inhibitors for the steel reinforcement. One of the advantages of these inhibitors is their cationic nature, which enables to remove chloride anions by electrochemical extraction simultaneously with electrochemical injection of inhibitor. Their inhibition efficiency was evaluated by means of polarization resistance of non-corroded and pre-corroded steel samples at different time intervals (15 min, 1 h and 24 h after addition of an inhibitor). The inhibition efficiency of 0.2 % solutions were compared with that of sodium nitrite. The results showed some inhibition capability of all studied compounds but only with nitrite on non-corroded steel were achieved values corresponding to an acceptable corrosion rate of steel reinforcement in concrete structures.

Keywords: Cationic organic inhibitor, inhibition efficiency, polarization resistance, sodium nitrite

1. INTRODUCTION

In steel-reinforced or prestressed concrete structures adequate corrosion resistance is usually provided by a passive layer on the steel surface resulting from the high alkalinity of the concrete environment [1]. A passive layer on steel surface in concrete structures could be damaged by action of two main factors. First of them is an ingress of chloride ions from de-icing salts or sea water. The other one is a reaction of alkaline pore solution with carbon dioxide from atmosphere. This process is known as a carbonation of concrete. Corrosion process following the depassivation of carbon steel reinforcement leads to cracking or spalling of a concrete cover [2].

Many inhibitors that improve corrosion resistance of carbon steel in concrete and that do not affect significantly the physical and mechanical properties of concrete are studied. Two principle groups of the corrosion inhibitors might be recognised.

Firstly, the preventive corrosion inhibitors which are usually admixed into the fresh concrete mixture. *Nitrite inhibitors*, especially calcium nitrite and sodium nitrite, have been extensively studied. They are not integrated in passive layer of carbon steel rebar but oxidise dissolved iron in oxidation state of II+ to passivating ferric oxide [3]. Several alternative preventive corrosion inhibitors such a *stannous chloride, sodium benzoate, salts of molybdate and borate, chromates and metasilicates* do not have an inhibition effect comparable with calcium nitrite [4, 5].

Secondly, the curative corrosion inhibitors which are designed to be applied onto the concrete surface by painting or spraying. They include s*odium mono-fluoro phosphate (MFP).* Its ability to penetrate into concrete is limited. The best results were achieved by using a MFP containing gel [2]. The laboratory studies showed that applying MFP onto concrete surface before the concrete structure is exposed to chloride containing environment the onset of active corrosion of reinforcement could be significantly prevented [2]. *Alkanolamines and amines* and their salts with organic and inorganic acids are promoted as vapour phase (VPI) or volatile (VCI) corrosion inhibitors with temporary corrosion protection of reinforcement. Typical compounds are diethanolamine, dimethylpropanolamine, monoethanolamine, dimethylethanolamine, monopropanolamine and triethanolamine [5].

Beside the application of corrosion inhibitors, the electrochemical methods of corrosion protection are well established for concrete structures protection or restoration, e.g. cathodic protection (CP), realkalization of carbonated concrete or electrochemical chloride extraction (ECE) [2]. All these techniques are based on cathodic polarization of the steel reinforcement. In the case of ECE, chloride ions migrate from the cathode (rebar) to an anode located at the surface of the concrete cover layer.

Electrical injection of corrosion inhibitors (EICI) is a relatively new technique that utilizes the ECE for transporting the inhibitors into concrete structure while chloride ions are being removed from concrete at the same time. Corrosion inhibitors that should be applicable by means of EICI must be positively charged. Positive charge enables their movement towards the negatively charged rebar surface in externally applied electrical field [6].

An inhibition efficiency of such EICI, e.g. quarternary ammonium and phosphonium salts [6], imidazoline quarternary ammonium salt (IQS) [7], tetrabulyammonium bromide salt [8], ethanolamine nitrate and guanidine carbonate [9, 10] and others is under intensive investigation, currently.

The paper assesses the corrosion inhibition efficiency of positive-charge corrosion inhibitors based on polyethylenimine and dimethyl-didecyl ammonium (bi)carbonate and it provides a comparison with the inhibition efficiency of sodium nitrite towards corroded or non-corroded carbon steel samples.

2. EXPERIMENTAL PART

2.1. Steel specimens

Strip-shaped carbon steel (30 x 350 mm) was used for the measurement. The strips were repeatedly immersed in the NaCl solution (concentration 25 g / l) to attain a corroded surface. Non-corroded surface of steel strips intended for comparative measurements was ground with P180 emery paper.

2.2. Organic corrosion inhibitors

Two commercial products differing in chemical composition of an active component were studied in this paper. They were selected because of their chemical stability in alkaline and neutral solutions and according to the producer’s declaration of their possible inhibition effect. The active components of these commercial products are dimethyl-didecyl ammonium (bi)carbonate (DDAC) and polyethylenimine (PEI), both at the concentration of 48 - 50 % (w / w). The recommended concentration of DDAC is between 0.10 - 0.25 %, the effective concentration of PEI is not specified.

2.3. Experimental arrangement

Polypropylene corrosion cells (30 ml) were fastened on the pre-corroded and non-corroded steel specimens. The cells were gradually filled with different solutions. The passivation capability in a highly alkaline environment corresponding to the concrete pore electrolyte was first studied on the non-corroded steel. The saturated solution of calcium hydroxide with pH value adjusted to 13 with sodium hydroxide was used. After 24 h the corrosion cells were emptied and filled with a new solution differing only in content of chloride anions (concentration of 15 g/l). After further 24 h the solution was replaced with a new one containing chloride anions and a corrosion inhibitor, too. Organic inhibitors were used in concentration 0.2% (w / w) and 1.0% (w / w) of an active component. Their inhibition effect on steel corrosion was compared with that of sodium nitrite. Nitrite was added to solutions in quantities corresponding to the ratio of molar concentrations 1:1 and 5:1 (nitrite anion to chloride anion) which means after conversion the concentrations 19.5 g / l and 97.3 g / l.

In defined time intervals (15 min, 1 h and 24 h after filling the corrosion cells with solution) reference electrode with counter electrode was immersed in solutions and polarization resistance was measured. As a reference electrode, the saturated calomel electrode (SCE) was chosen, platinum wire served as a counter electrode (CE). Polarization resistance was measured in range of ± 20 mV from an open circuit potential (E_{oc}) with a scan rate of 0.1 mV / s. The value of polarization resistance was subsequently determined from the slope of the line in the range of ± 5 mV from E_{oc}. Between measurements the corrosion cells were closed to prevent the sorption of carbon dioxide from the air.

3. RESULTS AND DISSCUSION

3.1. Corrosion behaviour of steel in model pore solution with chlorides

The polarization resistance of non-corroded steel specimen increased within the 24 hours of exposure (the lower is a value of polarization resistance the higher is a corrosion rate and conversely) in calcium hydroxide saturated solution. That proofs an ability of carbon steel to get passivated in the model pore solution containing no chloride ions. Final values ranged from 57 to 433 Ω·m^2 (184 Ω·m^2 on average). The passivation effect was also shown on open circuit potential. During 24 h, the values achieved ranged from -375 mV to -110 mV / SCE. According to ASTM-C 876 standard [11], the potentials were separated into three groups relating to probability of corrosion (see **Table 1**). Green color indicates low possibility of corrosion (about 10 %), grey values represent intermediate corrosion risk and red colour corresponds to potentials at which the steel corrodes with a probability of 90 %.

Table 1 Open circuit potential of steel specimens after 24 h exposure

	Open circuit potential (mV / SCE)							
Saturated solution; non-corroded steel	-158	-352	-180	-302	-376	-101	-115	-115
	-158	-162	-170	-180	-176	-121	-111	
Chloride solution; non-corroded steel	-577	-552	-458	-519	-496	-127	-402	-148
	-558	-558	-549	-548	-556	-525		
Chloride solution; pre-corroded steel	-566	-561	-576	-569	-543	-623	-606	-593
	-583	-572	-590	-574	-579	-585		

By replacing the saturated solution with another one containing chlorides, polarization resistance of steel decreased immediately by two orders of magnitude and remained relatively constant at the approximate value of 1 Ω·m^2 (non-corroded samples) or 0.35 Ω·m^2 (pre-corroded samples). Potentials of pre-corroded and non-corroded steel dropped to more negative values corresponding to the high corrosion risk (see the last two rows in **Table 2**).

3.2. Inhibition effect of nitrite

As expected, the inhibition effect of sodium nitrite was observed on the non-corroded samples. Replacement of the chloride solution with a solution containing nitrite resulted in a gradual rise of polarization resistance. After 24 h exposure, the value increased twenty times and exceeded 10 Ω·m^2. It represents a significant reduction of corrosion rate. By higher concentration of nitrite a better result was achieved - 35 Ω·m^2 (see filled bars in **Figure 1**). This value referred to the acceptable corrosion rate. The value of polarization resistance of about 30 Ω·m^2 is considered to be the threshold [12]. The different situation was identified on the pre-corroded steel samples. Neither longer exposure nor high concentration of nitrite in the solution elevated significantly the values of polarization resistance (see hatched bars in **Figure 1**). This result is consistent with the classification of nitrites as preventive corrosion inhibitors which can be admixed into fresh concrete mixture but which cannot be used for salinized concrete structures.

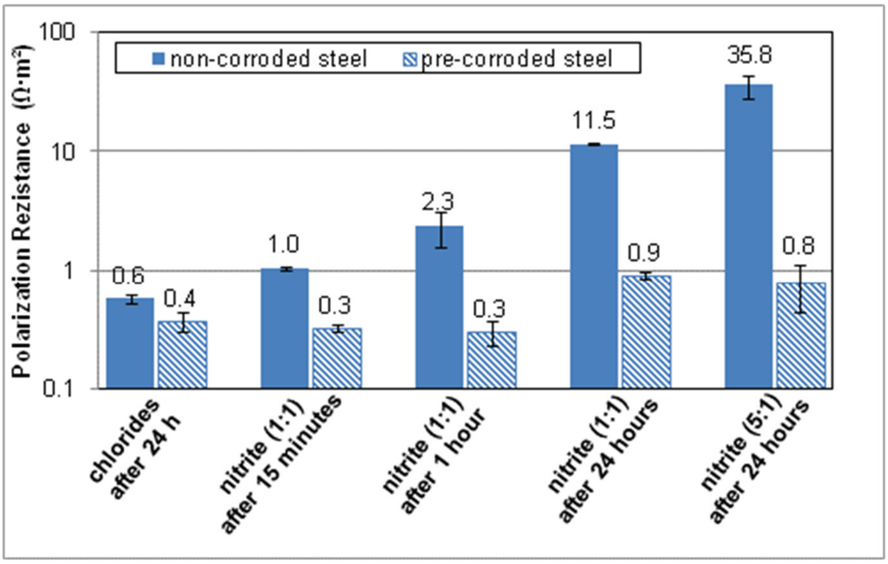

Figure 1 Inhibition effect of nitrite on carbon steel

The occurrence of nitrite ions in the solution was also reflected on an open circuit potential - a potential shift towards positive values (an increase of 87 mV on the non-corroded samples and 171 mV on the pre-corroded steel) was detected. However, the resulting values were -381 mV and - 392 mV on average. It means high corrosion risk according to ASTM standard but it is in conflict with polarization resistance results of the non-corroded steel. This discrepancy demonstrates the insufficiency of evaluation of corrosion resistance or a protective effect of inhibitors on steel by means of open circuit potentials. On the pre-corroded steel, the potential values were of -392 mV on average.

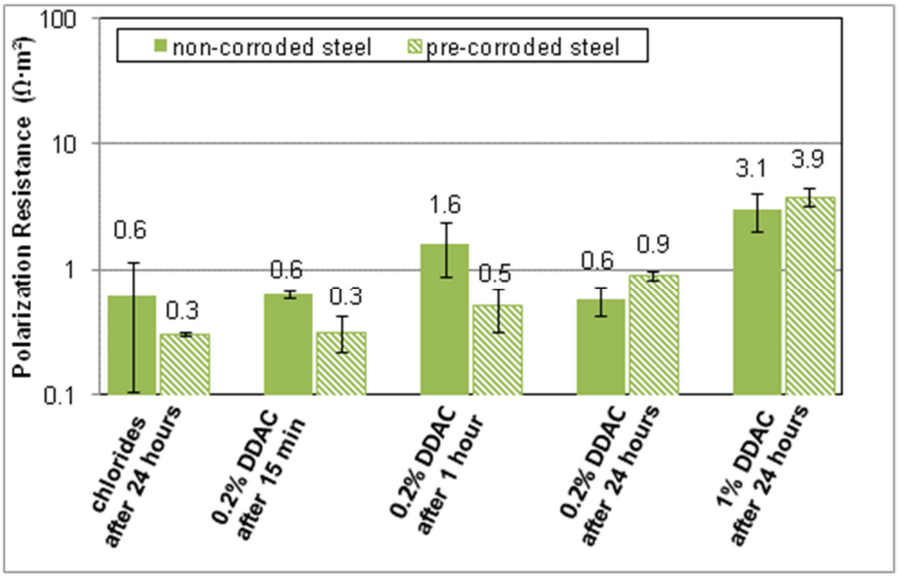

Figure 2 Inhibition effect of DDAC on carbon steel

3.3. Inhibition effect of cationic organic inhibitors

In the case of both organic inhibitors an unsatisfactory inhibition efficiency was observed. The values of polarization resistance ranged between 1-3 $\Omega\cdot m^2$ which is below an acceptable threshold. Nevertheless, there were some effects of inhibitors on corrosion of steel. Higher concentration of DDAC caused tenfold increase compared to chloride solution on pre-corroded steel (**Figure 2**). The effect was only threefold on the non-corroded steel. Inhibition efficiency of PEI was better on non-corroded steel at lower concertation than at higher one. Only the effect of higher concentration was observed on the pre-corroded samples (**Figure 3**).

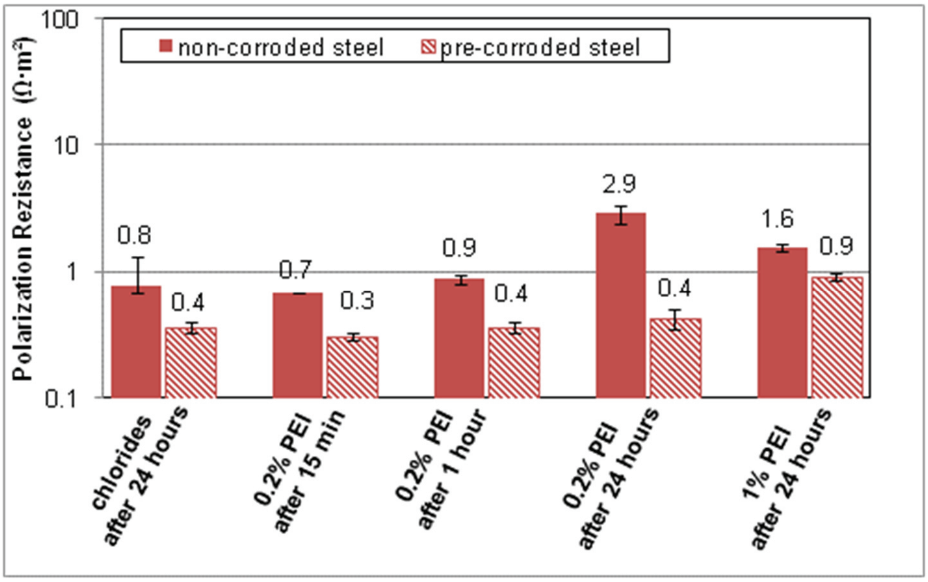

Figure 3 Inhibition effect of PEI on carbon steel

Average values of an open circuit potential after 24 h of the exposition are shown in **Table 2**. In the case of PEI they slightly rose but in the case of DDAC they moved oppositely and decreased towards -1 V on the pre-corroded steel.

Table 2 Average values of open circuit potential after 24 h exposure in solution with organic inhibitors

	Open circuit potential (mV / SCE)				
	Chlorides	**0.2 % DDAC**	**1 % DDAC**	**0.2 % PEI**	**1 % PEI**
Non-corroded steel	-469	-495	-536	-545	-580
Pre-corroded steel	-563	-727	-1088	-548	-532

4. CONCLUSION

The addition of all studied corrosion inhibitors to chloride containing solutions resulted in an increase of polarization resistance thus in a reduction of the corrosion rate. However, only the addition of nitrite in the combination with non-corroded steel led to the values corresponding to an acceptable corrosion rate of a steel reinforcement in concrete structures. A significant impact of surface condition on the type of corrosion inhibitor was also observed. In the case of sodium nitrite (preventive corrosion inhibitor) its corrosion efficiency on pre-corroded steel immediately disappeared and was lower than that of organic inhibitors with higher concentration of an active component. With these concentrations of organic inhibitors the polarization resistance kept being insufficient but independent from the surface condition.

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