Dedicated to the 80th anniversary of Professor Romanas Višomirskis

Corrosion behaviour of phosphated reinforcing steel in alkaline media contaminated with chloride ions

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The protective properties of three crystalline and one amorphous phosphate films on the surface of a reinforcing steel bar were examined in two different media: alkaline chloride solution and reinforcing concrete, used in the construction of bridges. Accelerated corrosion tests in a neutral salt spray chamber and immersion in a 5% NaCl solution were applied. Open circuit (corrosion) potential mapping and EIS were used for corrosion performance characterization, and AFM was used for surface morphology studies. According to the corrosion behaviour results obtained under various test conditions, the medium weight crystalline F11 phosphate film composed of Zn and Ca phosphates ensured the most effective protection of steel. Under the neutral salt spray chamber conditions, the reinforcing steel bars covered with different phosphate films in the concrete specimens exhibited very similar corrosion behaviour.

Key words: phosphate coating, reinforcing steel, corrosion, chloride, alkaline solution

INTRODUCTION

Steel bars embedded in concrete are protected from corrosion by a thin oxide layer formed on their surfaces because of highly alkaline environment of the surrounding concrete (pH $\approx$ 13). However, a breakdown of the passive film and, hence, corrosion can be stimulated either by carbonation, which reduces the pH of pure water to a non-protective level, or by the presence of significant quantities of chloride ions at the reinforcement level in the concrete. The most important cause of the initiation of corrosion of the steel bar is the ingress of chloride ions into the steel surface. Chlorides may depassivate steel even at high pH [1–6]. A variety of protective methods have been used to improve the corrosion resistance of reinforcing bars. One of them is phosphating, which is most widely used for a metal surface pre-treatment and finishing of ferrous and non-ferrous metals [7]. Combined with post-treatment with oil or wax, phosphate coatings are often applied for temporary corrosion protection of metal surfaces. It is generally accepted that the composition of a phosphate layer has a strong influence on its chemical stability. Authors [8–10] demonstrated that the elemental composition of the phosphate layer plays an important role in determining the alkaline stability of the layer. However, the major problem in using protective coatings in aggressive environments is the possibility of open porosity and pinholes in the coatings [11–13]. These local defects form direct paths between the corrosive environment and the substrate. The phosphate coating is an insulating film with pores. These pores induce the electrochemical

corrosion of the steel substrate in an aqueous solution. In general, lower porosity means lower corrosion rate of a substrate. The protection ability of the phosphate coating principally depends on its mechanical barrier [8].

The aim of the present work was to investigate under accelerated corrosion conditions the corrosion performance of phosphated reinforcing rebars in an alkaline solution containing chloride ions, and in structures of concrete used for the construction of bridges.

EXPERIMENTAL

Analytical grade chemicals were used to deposit the phosphate coatings and to prepare corrosion testing solutions. The saturated $Ca(OH)_2$ solution was filtered in order to avoid solid suspension and showed a pH value of ~13. Specimen corrosion (open circuit) potential (E_{corr}) surveys were carried out for 3 hours of the testing time (τ) using an Ag / AgCl reference electrode. Four types of phosphating solutions Likonda[1] were used for experiments (Table 1).

The working electrode was a rebar segment consisting of carbon steel (mass, %): C 0.2–0.29, Mn 1.2–1.6, Si 0.6–0.9, Cr $\leq$ 0.3, Ni < 0.3, S < 0.045, P < 0.040, Cu < 0.3. The steel samples were polished with No 600 SiC paper. A platinum plate was used as the auxiliary electrode.

Polarization measurements were performed with a PI-50-I potentiostat (Russia) under potentiodynamic conditions with a

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[1] Likonda – the trade mark of processes created at the Institute of Chemistry, Vilnius, Lithuania.

Table 1. **Phosphating solutions and phosphate coatings characteristics**

Phosphate coating type	Composition of solution, M	Composition of coating (XRD data)	Coating weight, g m⁻²	Grain size, μm	ΔE_{Me} *, mV/10 min
Likonda F1 (F1)	Zn^{2+} – 0.17, PO_4^{3-} – 0.34 NO_3^- – 0.14 NO_2^- – 0.0025	$Zn_3(PO_4)_2 \cdot 4H_2O$ $Zn_2Fe(PO_4)_2 \cdot 4H_2O$	6–8	45–50	50–70
Likonda F11 (F11)	Zn^{2+} – 0.12 PO_4^{3-} – 0.34 NO_3^- – 0.14 Ca^{2+} – 0.05 NO_2^- – 0.0025	$Zn_3(PO_4)_2 \cdot 4H_2O$ $Zn_2Ca(PO_4)_2 \cdot 2H_2O$	3–5	10–15	100–120
Likonda F44 (F44)	Zn^{2+} – 0.17, PO_4^{3-} – 0.34 NO_3^- – 0.14 Ni^{2+} – 0.003	$Zn_3(PO_4)_2 \cdot 4H_2O$ $Zn_2Fe(PO_4)_2 \cdot 4H_2O$ $Ni_3(PO_4)_2 \cdot 2H_2O$	10–12	25–30	80–100
Likonda FA50 (FA50)	PO_4^{3-} – 0.16 MoO_4^{2-} – 0.0012	–	0.6–0.8	Amorphous	20–30

* ΔE_{Me} – the difference in values between the steel dissolution potential and those of completion of phosphate film growth (indicator of the film porosity).

potential scan rate of 0.2 mV s⁻¹. Corrosion currents (I_{corr}) of the samples investigated in a saturated $Ca(OH)_2$ + 1 M NaCl solution were determined from Tafel line extrapolation. The polarization resistance (R_p) values were determined from linear polarization measurements, which were performed between ±10 mV around the corrosion potential and from EIS studies.

For the investigation of the corrosion behaviour of steel in concrete structures, cylindrical concrete specimens (10 cm in diameter and 15 cm in height) containing a reinforcing steel bar (rebar) segment were prepared from cement of 320 kg/m³, following the procedure and using materials applied for the construction of bridges [14]. The formulation for the reinforcing concrete specimens used in kg/m³ was the following: cement – 450, sand – 665 and gravel – 1100. The water / cement ratio was 0.41. The reinforcing steel bars were 15 cm long with a diameter of 0.95 cm and had an exposed area of about 20 cm². The concrete specimens were exposed to tap water (cured) for 27 days. One set did not have a phosphate layer and the second one was phosphated in Likonda F1, F11, F44, FA50 solutions (Table 1). E_{corr} mapping (vs Ag / AgCl) was carried out for three parallel samples and the average E_{corr} values were presented.

Assuming that the phosphate coating was electrochemically inert at low anodic over-potentials, the porosity of the coating was calculated using the following equation [11–15]:

$$F = (R_{p,m} / R_p) \ 10^{-|\Delta E_{corr}|/b_a},$$ (1)

where F is the total coating porosity, $R_{p,m}$ is the polarization resistance of the base material R_p – the measured polarization resistance, ΔE_{corr} – the difference between the corrosion potentials and b_a is the anodic Tafel slope of the base material. The reinforcing steel itself has the anodic Tafel slope b_a = 70 mV and polarization resistance $R_{p,m}$ = 1.21–1.34 KΩ. The potentials of the phosphated reinforcing steel were measured after 1 h of its immersion in the saturated $Ca(OH)_2$ + 1 M NaCl solution.

Electrochemical impedance spectroscopy (EIS) was applied in order to evaluate the corrosion state of the steel / concrete system. The impedance measurements were carried out within a frequency range from 10⁻³ to 20 KHz using a Zahner (Germany) IM6 Impedance Spectrum Analyser. The perturba-

tion signal amplitude was ±10 mV. A three-electrode arrangement was used. The electrochemical parameters normally used to characterize the corrosion behaviour of the reinforcing steel in concrete were monitored periodically over the course of approximately 4.5 years.

Surface morphology studies were carried out with an AFM, Explorer (VEECO-Thermo microscopes) scanning probe microscope at atmospheric pressure and room temperature in a contact mode. A Si_3N_4 cantilever with the force constant of 0.032 N m⁻¹ was used, and the resolution of the images obtained was 300 × 300 pixels.

The phases and composition of the phosphate deposits were analysed by X-ray diffraction XRD (DRON-2) using CuK_α-subradiation (50 kW, 150 mA).

All the experiments were performed at ambient temperature (20 ± 2 °C).

RESULTS AND DISCUSSION

Tests in alkaline solution

A detailed characterization of the properties of the investigated phosphate coatings on steel was presented in our previous study [16]. The phosphate films differed in their structure and composition (Table 1). With reference to the AFM images presented in Fig. 1, it can be seen that phosphate coatings F1, F11 and F44 (Fig. 1 a, b, c), possessed crystalline structures with the grain size between 10 and 50 μm, while FA50 film appeared to be amorphous (Fig. 1 d). The latter coating was the lightest one (0.6–0.8 g m⁻²), while F1 (6–8 g m⁻²) and F11 (3–5 g m⁻²) corresponded to the medium-weight, and F44 (10–12 g m⁻²) – to a heavy-weight phosphate coating. According to the performed XRD analysis, crystalline film F11 was composed of Zn and Ca phosphates, while films F1 and F44 contained Zn and Ca phosphates, besides, F44 layer additionally contained Ni phosphate (Table 1).

Since the phosphate coatings are porous, corrosion of steel substrate in aggressive media can take place. In general, lower corrosion rates are related to the lower porosity of the film. At the initial stage of steel phosphating, the dissolution of the base metal occurs, which is accompanied by a decrease in the value
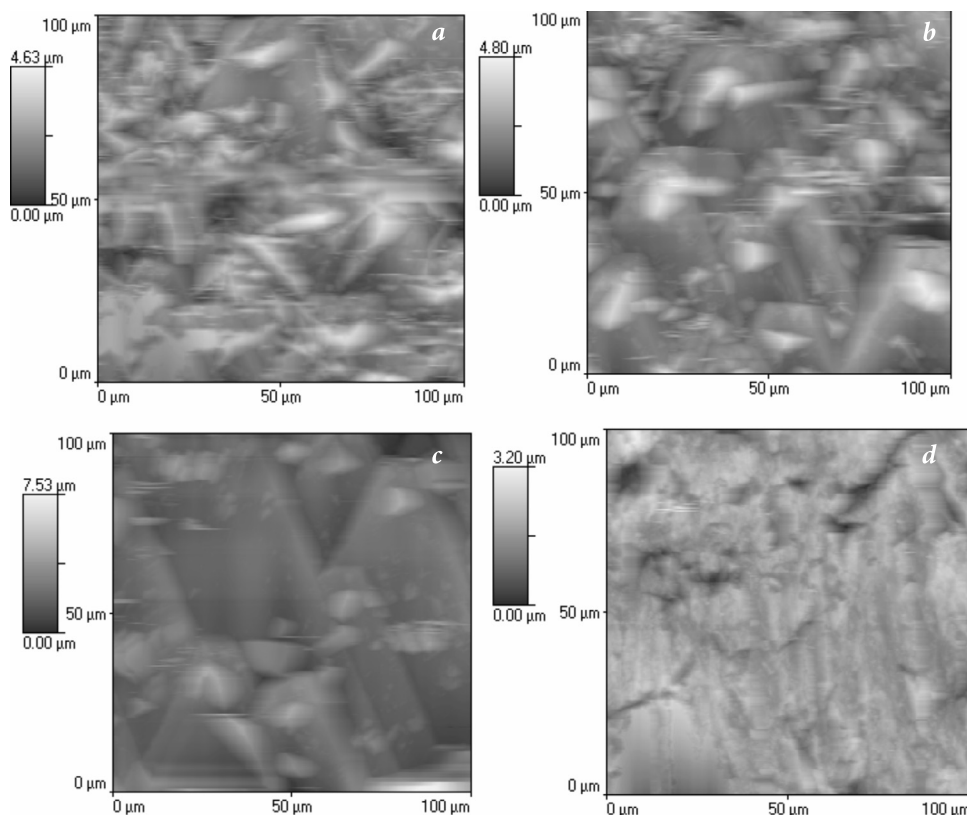
Fig. 1. AMF images of the phosphate films obtained in various solutions: (*a*) F11, (*b*) F44, (*c*) F1, (*d*) FA50

of steel potential E_{Me}. When the growth of the film is completed, E_{Me} reaches its constant value. The maximum difference in values between the metal dissolution potentials and those of the completion of the phosphate coating growth (ΔE_{Me}) is an indicator of the film porosity [8, 16]. A higher margin of ΔE_{Me} corresponds to a lower porosity of the phosphate coating. The ΔE_{Me} for the investigated phosphate films were determined and it appeared that the layers deposited in solution F11 possessed the highest ΔE_{Me} values (~100–120 mV/10 min), which implies the lowest porosity from the all-crystalline phosphate films studied. The highest porosity could be attributed to F1 coating, as its ΔE_{Me} values were 50–70 mV/10 min (Table 1).

Since Cl⁻ ions promote steel corrosion, the protective properties of phosphate films were investigated in a saturated $Ca(OH)_2$ solution containing 1 M NaCl by monitoring the steel electrode corrosion potentials. The potential mapping (E_{corr}–τ) plots of the phosphated steel bars during the initial stages of corrosion are presented in Figure 2. The E_{corr} values of all the phosphated steel electrodes after 3 hours of exposure to the test solutions were by 50 to 100 mV more positive as compared with those of the non-covered examples.

The corrosion current (I_{corr}) values were determined from Tafel line extrapolation to E_{corr} and the obtained results are list-

ed in Table 2. The uncovered steel electrode exhibited two- or three-fold higher I_{corr} values as compared to those of the phosphated samples. The electrodes with all the crystalline phosphate coatings possessed very close I_{corr} values varying between $1.8 \cdot 10^{-6}$ and $2.9 \cdot 10^{-6}$ A cm⁻², while the amorphous one (FA50 coating) exhibited higher (~$4.1\ 10^{-6}$ A cm⁻²) I_{corr}, nevertheless, these values were lower with respect to a non-phosphated sample ($5.9\ 10^{-6}$ Acm⁻²).

EIS measurements of the phosphated steel electrodes were carried out with the aim to determine the polarization resistance, which is in the inverse proportion to the corrosion current density. The R_p values were determined from the equivalent circuit parameters obtained from an experimental data fitting procedure and are presented in Table 2, together with individual E_{corr} values of the same samples. The experimental data were fitted assuming that an equivalent circuit consisted of solution resistance and R_p was in parallel with a constant phase element (CPE), the impedance of which is given by $Z_{CPE} = 1/C(j\omega^{-n})$ [17]. The factor n is close to 1 (0.89–0.95).

In addition, R_p was determined from the linear polarization measurements (data are given in Table 2). Both of the methods applied yielded very close R_p values, which varied in the range from ~2.5 KΩ cm² to 9.39 KΩ cm². All the determined R_p values

Table 2. **The electrochemical parameters of steel bar with / without phosphate coating in saturated $Ca(OH)_2$ + 1 M NaCl solution**

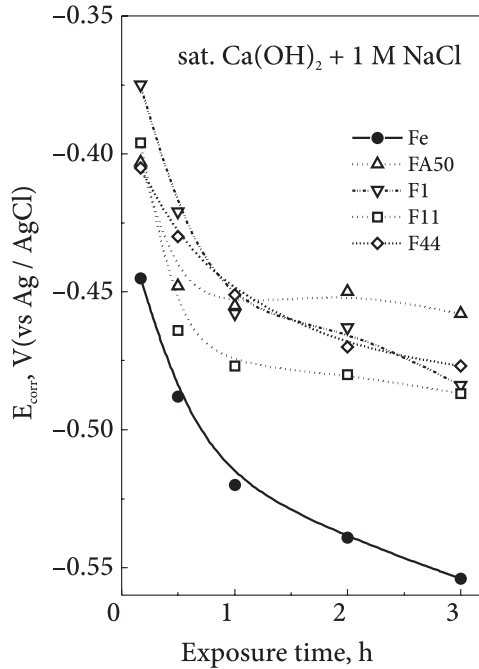| Coating	I_{corr} / A cm⁻²	R_p / Ω cm² (d.c.)	R_p / Ω cm² (EIS)	E_{cor}, V	*Porosity*, % (average from Tafel and EIS R_p values)
Without coating	$5.9 \cdot 10^{-6}$	1340	1210	−0.52	–
F1	$2.6 \cdot 10^{-6}$	5010	6220	−0.465	3.6
F11	$1.8 \cdot 10^{-6}$	8200	9390	−0.451	1.8
F44	$2.9 \cdot 10^{-6}$	6720	8460	−0.460	2.5
FA50	$4.1 \cdot 10^{-6}$	2600	2490	−0.478	5.7

Fig. 2. Dependence of the corrosion potential E_{corr} of reinforcing steel bar coated with a phosphate film in a saturated Ca(OH)$_2$ + 1 M NaCl solution on the time of exposure

for steel electrodes with the phosphate coatings were higher with respect to the sample without a coating. The R_p values obtained for amorphous coating FA50 were only by two times higher, while the other crystalline coatings possessed four- to eight-fold higher R_p values in comparison to the non-phosphated samples.

The corrosion reactions are initiated at the phosphate coating-substrate interface; therefore, it is important to determine the porosity in order to estimate the overall corrosion resistance of the coated materials. The obtained R_p values of the phosphated samples enabled to calculate the porosity of the coating using equation (1), and the results obtained are presented in Table 2. Having analysed the results of the coating porosity achieved by two independent methods, it can be observed that the indicator of the film porosity ΔE_{Me} (Table 1) and porosity F (%), obtained from equation (1) (Table 2) perfectly correlated. The highest values of ΔE_{Me} – 100–120 mV (implying the lowest porosity) and the lowest values of $F < 2\%$ were determined for the crystalline F11 coating. In general, the presented data indicate that the crystalline phosphate coatings were less porous in comparison with the amorphous FA50 coating.

A low value of porosity is beneficial to the corrosion resistance of the coating that acts as a physical barrier against corrosive agents.

The data obtained indicate that all the phosphate films studied protect steel from corrosion in alkaline solutions even when 1 M of Cl⁻ ions is present in the corrosion environment. Therefore, these coatings were tested in concrete structures, which are usually used for bridge construction.

Tests in concrete

The corrosion behaviour of the phosphated steel bars in concrete has been investigated by a concrete cylinder test in a neutral salt spray chamber (35 ± 2 °C) as well as by immersion of the cylin-

der in a 5% NaCl solution (20 ± 2 °C). The corrosion of steel under the salt spray conditions and in the NaCl solution is induced by Cl⁻ ions. The corrosion potentials of the rebar were monitored for 4.5 years, and the results are presented in Figures 3 and 4.

None of the corrosion potential values uniformly defines the limit between passive and active corrosion behaviour and the corrosion potentials that are related directly to the corrosion rate. However, it is confident to compare E_{corr} values of the steel reinforcement exposed to the same conditions (temperature, humidity), and while comparing these values interdependently, it is reasonable to consider the metal state in the concrete structure.

The results of the steel rebar corrosion potential mapping during the concrete sample immersion in the 5% M NaCl solution are presented in Fig. 3. Phosphate film F11 exhibited the best corrosion protective properties under these conditions, as only the steel coated with this film even after a period of 4.5 years possessed more positive potential values as compared to those of the uncoated rebar (Fig. 3). The same films also possessed the lowest porosity as it had been discussed previously. Meanwhile, after 4.5 years of exposure, the rebars coated with amorphous FA50 and crystalline F44, F1 films exhibited E_{corr} values very similar to those of bare steel, which implies that the corrosion protection provided by these coatings is insufficient.
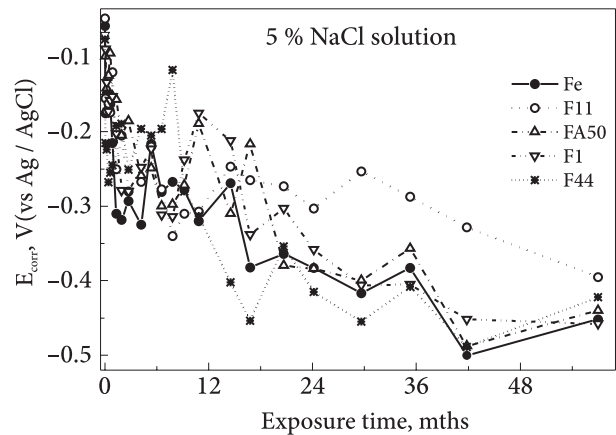

Fig. 3. Corrosion potential E_{corr} of reinforcing steel bar coated with a phosphate film in concrete specimen, exposed to 5% NaCl solution at 20 ± 2 °C
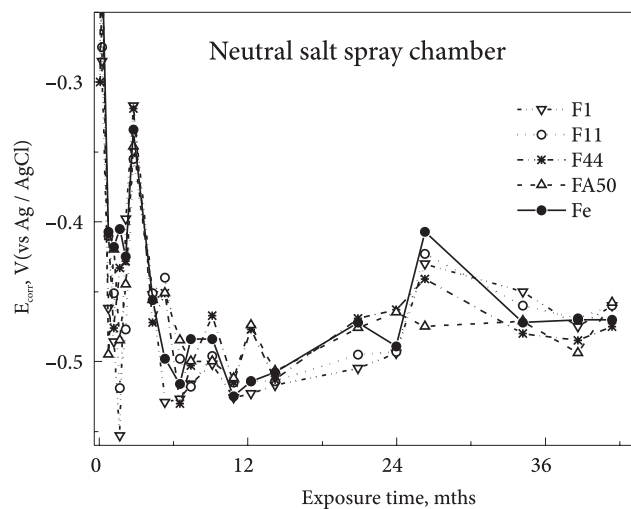

Fig. 4. Corrosion potential E_{corr} of reinforcing steel bar coated with a phosphate film in concrete specimen, exposed to neutral salt spray chamber at 35 ± 2 °C

The accelerated corrosion tests of the phosphated rebar in concrete cylinders were carried out in the neutral salt spray chamber. The potential mapping results under these conditions are presented in Fig. 4. It seems that the neutral salt spray chamber conditions were too aggressive for the phosphated rebar in concrete, as during the first several months of exposure all the investigated samples reached $\sim$ –0.5 V (Ag / AgCl) potential values (Fig. 4), which did not change significantly during the following two and a half years. There were no considerable differences in E_{corr} values and for the various phosphated coatings under these accelerated test conditions.

In addition to E_{corr} mapping, EIS measurements were carried out with the concrete cylinders immersed into the 5% NaCl solution with the aim to determine the polarization resistance, which is in the inverse proportion to the corrosion current density. The R_p values were determined from the equivalent circuit parameters obtained from an experimental data fitting procedure and are presented in Fig. 5. These data suggest that the beneficial effect of the phosphate films on the rebar corrosion became pronounced only up to half a year of sample exposure, as the R_p values of the phosphated samples determined were higher with respect to those of the uncoated steel. However, after 1.5 years of exposure only the rebar with film F11 exhibited significantly higher R_p values (0.84 MΩ cm^2), while all the rest systems possessed R_p close to 0.2–0.4 MΩ cm^2. After 4.5 years of exposure all the systems possessed R_p close to 0.025–0.09 MΩ cm^2.
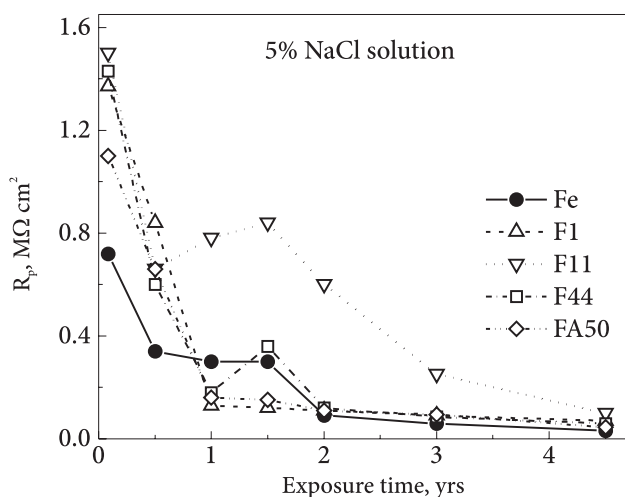

Fig. 5. Dependence of the polarization resistance R_p of reinforcing steel bar coated with a phosphate film in concrete specimens exposed to 5% NaCl solution

The fluctuations in R_p and E_{corr} values are common phenomena for the rebar corrosion in the concrete investigations and are related, most probably, to the repassivation of the corroded areas. The obtained data indicated that phosphate coating F11 provided the most prolonged corrosion protection of all the steel bars samples in concrete used for bridge construction.

Summarizing the obtained results, it can be stated that the thickness of the phosphate coating is of none importance in determining the protective properties of reinforcing steel, while it is obvious, that less porous phosphate coatings yield a higher protection level of reinforcing steel corrosion in concrete.

CONCLUSIONS

The protective properties of three crystalline and one amorphous phosphate films on steel surface were examined in alkaline media and concrete specimens used for the construction of bridges. According to the corrosion behaviour of the rebar electrode in a saturated Ca(OH)$_2$ solution containing 1 M chloride and the performance of the reinforcing concrete specimens in a NaCl media, the most effective protection of steel was exhibited by the crystalline F11 phosphate film.

The thickness of the phosphate coating was not an important factor in determining the protective properties of the reinforcing steel, while its porosity was very important. Less porous phosphate coatings yielded higher protection level of the reinforcing steel corrosion in concrete.

All the phosphated rebars in the concrete specimens exhibited very similar corrosion behaviour under neutral salt spray chamber conditions and the protection of steel with the phosphate films was not effective enough.

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**FOSFATUOTOS PLIENINĖS ARMATŪROS KOROZINĖ
ELGSENA CHLORIDO JONAIS UŽTERŠTOJE ŠARMINĖJE
APLINKOJE**

S a n t r a u k a

Plieninės armatūros, padengtos trijų rūšių kristalinėmis ir amorfine dangomis, korozinė elgsena tirta chloridiniuose šarminiuose tirpaluose bei gelžbetoniniuose pavyzdžiuose, pagamintuose iš betono, naudojamo tiltų statyboje. Gelžbetoninių pavyzdžių paspartinti koroziniai tyrimai atlikti patalpinus juos į 5% NaCl tirpalą bei druskos rūko kamerą. Atviros grandinės potencialo matavimai ir EIS (elektrocheminio impedanso spektroskopijos metodas) naudoti korozijos procesui apibūdinti, AFM – paviršiaus morfologiniams tyrimams. Tyrimai parodė, kad 5% NaCl tirpale geriausiai plieną nuo korozijos apsaugo vidutinio svorio, sudaryta iš Zn ir Ca fosfatų, kristalinė F11 danga. Tuo tarpu druskos rūko kameroje visų fosfatuotų pavyzdžių korozinė elgsena buvo panaši.