Efficiency of steel corrosion inhibitor calcium nitrite in alkaline solutions and concrete structures

Olga Girèienë*,

Meilutë Samulevièienë,

Aloyzas Sudavièius,

Rimantas Ramanauskas

Institute of Chemistry, A. Goštauto 9,
LT-01108 Vilnius, Lithuania
E-mail: olgag@chi.lt

Leontij Lapuchin

Tilsta Bridge Building Co.,
Granito 6, LT-2028 Vilnius, Lithuania

The corrosion behaviour of steel in two different media, alkaline chloride solution and reinforced concrete used in bridge building, with and without the inhibitor calcium nitrite was investigated. Accelerated corrosion tests in neutral salt spray and CO_2 chambers, as well as immersion in 5% NaCl solution were applied. Open circuit potential mapping and EIS were used for corrosion performance characterization, while XPS was employed for corrosion product analysis and AFM for surface morphology studies. Introduction of calcium nitrite in both study media reduced the corrosion rate of steel reinforcement. The inhibitory effect of nitrite manifested through the improvement of protective properties of the corrosion product (oxide layer) film.

Key words: corrosion inhibitor, reinforcing steel, concrete, calcium hydroxide, oxide layer

INTRODUCTION

Reinforcement corrosion is one of the major causes of degradation in concrete structures. Concrete normally provides reinforcing steel with excellent means of protection against corrosion. However, the pollution of concrete by aggressive species such as chloride and carbon dioxide leads to a decrease in pH and a breakdown of the passive film. It results in the corrosion of the steel-reinforcing bar (rebar) and, in the long term, the deterioration of the concrete.

The central reaction in corrosion process of steel is over-simplified by:

$$Fe° \rightarrow Fe^{++} + 2e^-. \quad (1)$$

The reactions affecting corrosion in concrete are numerous and far more complicated [1]. A deeper consideration reveals that oxygen has the most detrimental effect, while chloride is only the catalyst. Ferrous ions are soluble enough to travel some distance, especially under corrosion conditions in the presence of chloride ions and reduced pH. The ferrous ions would be easily oxidized by air to ferric ions and precipitate as one of several oxides [1]:

$$xFe^{++} + yO_2 + H_2O \rightarrow Fe_3O_4, Fe_2O_3, Fe(OH)_3, Fe(OH)_3 \cdot 3H_2O. \quad (2)$$
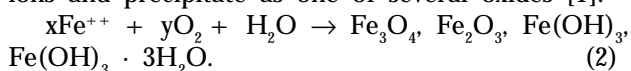
CO_3^{2-} ions are less aggressive in corrosion reactions as compared with chloride ions [1–3]. The carbonization depth in the cement mass was measured in works [2, 3]. The effect of carbon dioxide in reducing the pH of concrete manifests because of the reaction

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O, \quad (3)$$
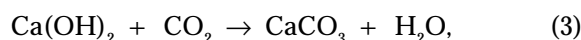
which makes it an accessory to corrosion. In practice, however, carbonization of concrete causes problems (by reducing the pH and the protection normally afforded by concrete) only when the cover on the steel is shallow and concrete is porous [1–3].

Various ways to protect the rebar in concrete can be envisioned. One of the common corrosion prevention practices is to incorporate inhibitors in potentially corrosive environments. The effects of an inhibitor are to raise the level of chloride ions necessary to initiate corrosion and to decrease the rate of corrosion even if it starts [1–9].

In the 1980s, numerous corrosion studies documented the corrosion inhibiting properties of calcium nitrite. Studies of the inhibitors have shown that calcium nitrite, being an anodic inhibitor, modifies the oxide film on a steel bar to be more protective rather than the film that naturally forms in concrete. The inhibitive action of calcium nitrite depends on its reaction with Fe^{2+} ions according to the following reaction [1, 5, 9]:

$$2Fe^{2+} + 2OH\downarrow + 2NO_2 \rightarrow 2NO\uparrow + Fe_2O_3 + H_2O. \quad (4)$$
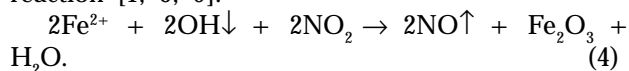
Calcium nitrite competes with the chloride ions for the ferrous ions produced in concrete and incorporates them into a passive layer on the iron surface, thus preventing further corrosion [9]. Numerous researchers have also documented that nitrite incre-

ases the chloride content at which pitting and active corrosion initiate for steel in concrete [1, 5–8].

A simple way to investigate the corrosion process of steel is to substitute limewater for solid concrete [10–15]. Small rebar specimens can be tested in various solutions quickly and extensively with laboratory instrumentation. However, making predictions about service life of field concrete based on time to corrode in limewater is not feasible, because the chemical environment a round a rebar in limewater is significantly different from that in concrete.

The aim of the present work was to evaluate $Ca(NO_2)_2$ as a possible inhibitor for the concrete used in bridge production and to compare the corrosion behaviour of steel rebar in an alkaline solution containing an inhibitor, as well as in concrete samples under conditions of the accelerated corrosion test. Open circuit potential mapping and electrochemical impedance spectroscopy (EIS) were applied for corrosion performance characterization, while XPS was used for corrosion product analysis and AFM for surface morphology studies.

EXPERIMENTAL

Test in alkaline solution
Analytical grade chemicals were used to prepare corrosion test solutions. Preliminary analysis of the inhibiting effect of the study substances was carried out in a saturated calcium hydroxide solution containing a chloride at a concentration of 0.1 M. The saturated $Ca(OH)_2$ solution was filtered to avoid solid suspension and showed a pH value of ~13. Open circuit potential (E_{corr}) surveys of specimens were carried out at regular intervals for 60 min and 7 days of testing time (τ) using an Ag / AgCl reference electrode.

Polarization measurements were performed with a PI-50-I potentiostat (Russia) under potentiodynamic conditions with a 0.5 mV s^{-1} potential scan rate. The working electrode was a disk 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. The auxiliary electrode was a platinum plate.

Test in concrete
The cylindrical concrete specimens (10 cm in diameter and 15 cm high) containing a rebar segment were prepared using cement of 320 kg/m^3 weight. The formulation for the reinforced concrete specimens used in kg/m^3 was: cement 450, sand 665, gravel 1100. The water / cement ratio was 0.41. One set of concrete samples was without the inhibitor; a next one contained 16 g/dm^3 of $Ca(NO_2)_2$. The percentage of the inhibitor referred to the weight of cement was added to the mixture. The rebar segments and the

working electrodes for electrochemical measurements were made from the same steel. They were 15 cm long, had a diameter of 0.95 cm and presented an exposed area of about 20 cm^2. The concrete specimens were exposed to a tap water (cured) for 27 days.

The corrosion potential (E_{corr}) was measured with the same potentiostat and Ag / AgCl reference electrode. The potential mapping was carried out for three parallel samples, and the average E_{corr} values are presented.

Electrochemical impedance spectroscopy (EIS) was applied trying to evaluate the corrosion state of the steel / concrete system. Impedance measurements were carried out within a frequency range from 10^{-3} to 20 KHz using a Zahner (Germany) IM6 impedance spectrum analyzer. The perturbation signal amplitude was ± 10 mV. A three-electrode arrangement was used.

The electrochemical parameters normally used to characterize the corrosion behaviour of reinforcing steel in concrete were monitored periodically for approximately 27 months.

Surface analysis
The XPS spectra were recorded with an Escalab MK spectrometer (Great Britain) using X-radiation of MgK_α (1253.6 eV, pass energy of 20 eV). To obtain depth profiles, the samples were etched in the preparation chamber with ionized argon at a vacuum of 5×10^{-4} Pa. An accelerating voltage of *ca.* 1.0 kV and a beam current of 20 μA cm^{-2} were used, which corresponded to an etching rate of *ca.* 2 nm min^{-1}. The Fe 2p$_{3/2}$, O 1s, Cl 2p, N 1s, Ca 2p$_{3/2}$ spectra were recorded when investigating the elemental composition of the coatings. Empirical elemental sensivity factors were taken from the literature, and the obtained spectra were compared with the standard ones.

Surface morphology studies were carried out with an AFM by an Explorer (VEECO-Thermo microscopes) scanning probe microscope at atmospheric pressure and room temperature in a contact mode. A Si$_3$N$_4$ cantilever with the force constant of 0.032 N m^{-1} was used and the resolution of the images was 300 $\times$ 300 pixels.

RESULTS AND DISCUSSION

Test in alkaline solution
The inhibitory effect of the following substances: calcium nitrite, trisodium phosphate, 1, 2, 3-benzotriazole, calcium glycerophosphate and sodium tetra borate on steel corrosion in alkaline media was investigated in our previously studies [17]. The inhibitor *vs.* chloride ion ratio [Inh] / [Cl] in the working solution (a saturated $Ca(OH)_2$ + 0.1 M NaCl) varied from 0.005 to 1. The preliminary results have shown

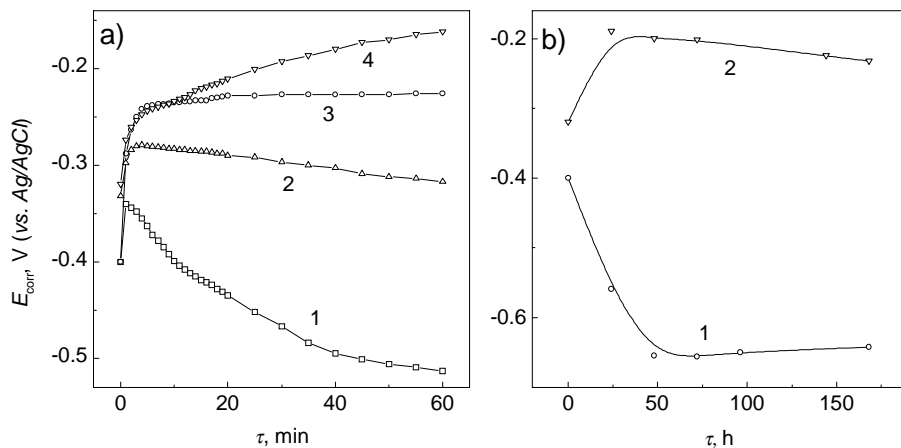**Fig. 1.** Dependence of corrosion potential of steel E_{corr} in a saturated $Ca(OH)_2$ + 0.1 M NaCl solution on the time of exposure 60 min (*a*) without (1) / with (2–4) $Ca(NO_2)_2$: 2 – 0.005 M, 3 – 0.01 M, 4 – 0.05 M and 7 days (*b*) without (*1*) / with (*2*) 0.05 M $Ca(NO_2)_2$

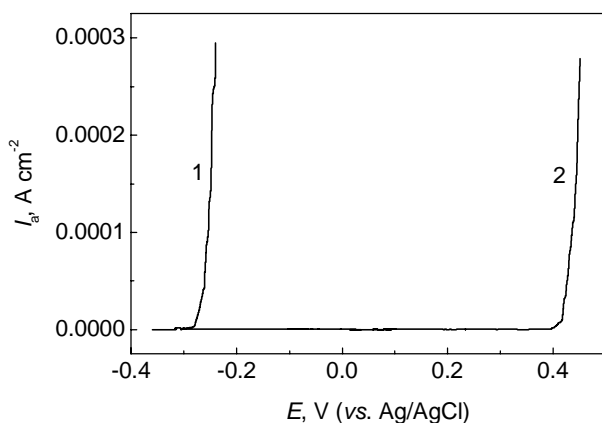**Fig. 2.** Anodic polarization curves of steel electrodes (preliminary oxidized 1 hour in the working solution) in a saturated $Ca(OH)_2$ + 0.1 M NaCl solution either in absence (*1*) or in the presence (*2*) 0.05 M $Ca(NO_2)_2$

that the most effective inhibition properties were exhibited by $Ca(NO_2)_2$.

The potential mapping (E_{corr}–τ) plots of the steel electrode for 60 min and a 7-day exposure to a solution containing various concentrations of calcium nitrite are presented in Fig. 1a and b, respectively. The E_{corr} values of steel in the solution containing the inhibitor were evidently more positive with respect to those registered in a solution without inhibitor (blank solution). The steel electrode potential after 7 days of exposure to the blank solution (Fig. 1b, curve 1) was up to 0.4 V more negative in comparison to those obtained in the solution with 0.05 M $Ca(NO_2)_2$ (Fig. 1b, curve 2). The potential mapping data imply that 0.05 M of calcium nitrite in chloride ion containing alkaline solution is an effective steel inhibitor.

It has been determined in several studies that $Ca(NO_2)_2$ is an anodic inhibitor, which can modify the oxide film on the steel surface to be more protective than the film that is naturally formed in concrete [1, 7, 9]. The protective properties of the oxide

film formed on the steel surface in alkaline media containing an inhibitor were investigated by means of Cl⁻ induced film breakdown potential (E_{pit}) measurements. The anodic polarization curves of preliminarily passivated samples in the blank solution and in the solution with inhibitor are presented in Fig. 2. The formation of oxide (passive) layers was carried out during one hour of steel electrode immersion in the working solution, while the anodic polarization was measured later on in the same medium. The difference between E_{pit} and E_{corr} (E_{pit}–E_{corr}) in the blank solution was determined to be ~0.13 V, while in the presence of inhibitor this difference was ~0.75 V. The data obtained imply that the protective properties of the oxide film formed in a solution containing $Ca(NO_2)_2$ were significantly higher with respect to inhibitorless ambient formed ones.

The composition and thickness of oxide films on the steel surface were examined by means of XPS measurements. Fe $2p_{3/2}$, O 1s, N 1s and Ca $2p_{3/2}$ peaks were analyzed after surface sputtering with Ar⁺ ions for an increasing period of time. The depth profiles of oxygen and iron of the samples are presented in Fig. 3a. The data suggest that the thickness of the oxide film formed after 24 hours of steel exposure to a saturated $Ca(OH)_2$ + 0.05 M $Ca(NO_2)_2$ solution reached *ca.* 2–3.5 nm. An additional introduction of 0.1 M NaCl into this solution lowered the thickness of the oxide layer by *ca.* 1.7–
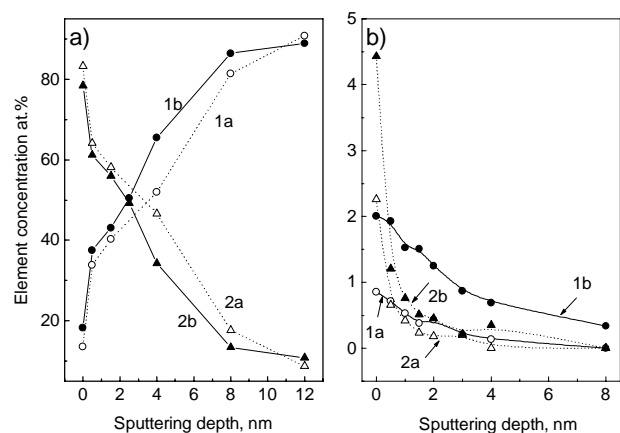

Fig. 3. Depth profiles (XPS data) of Fe, O (*a*) and Ca, N (*b*) for oxide films on steel surface formed during 24 hours exposure to a saturated $Ca(OH)_2$ + 0.05 M $Ca(NO_2)_2$ solution without (*1a, 2a*) and with (*1b, 2b*) 0.1 M NaCl

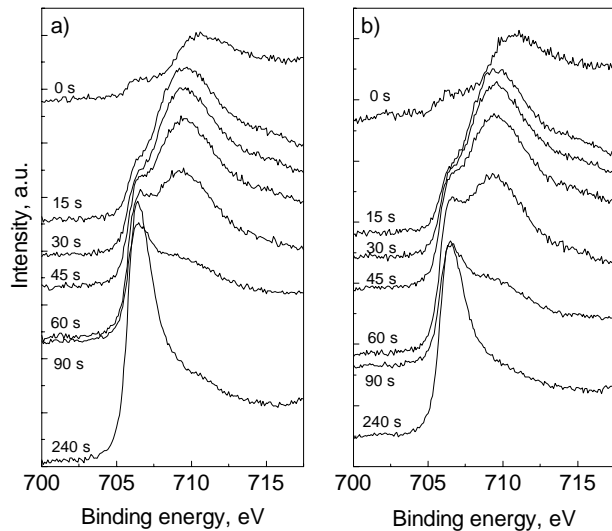**Fig. 4.** Fe2p$_{3/2}$ XPS spectra of the oxide film formed (24 h) on steel surface obtained in a saturated Ca(OH)$_2$ + 0.05 M Ca(NO$_2$)$_2$ solution without (*a*) and with (*b*) 0.1 M NaCl after various sputtering times

2.4 nm. A film of oxide 1.7 to 5.0 nm thick is thought to form a barrier layer to corrosion on bare steel [1].

The presence of Cl⁻ ions in the test media influenced the composition of the oxide film as well. The ratios of the surface concentrations of Fe and O in solution free from Cl⁻ ion were determined to be 2:1 and 1.4:1 in the external and internal parts of the oxide layer, respectively. These ratios, along with
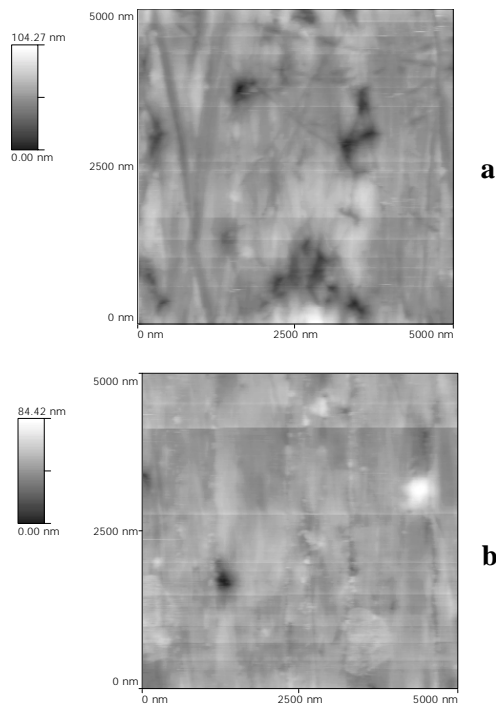
the binding energy values of Fe 2p$_{2/3}$ (Fig. 4a), imply that the oxide film contained FeOOH (corresponding binding energy of Fe – 710.8 eV) and Fe$_2$O$_3$ (corresponding binding energy of Fe – 711.0 eV). While, in the presence of Cl⁻ ions in solution, the Fe / O ratios varied between 1:1.6 and 1:1.3, suggesting that the oxide film consisted of Fe$_2$O$_3$ and Fe$_3$O$_4$ (binding energy of Fe in the latter compound was 711.3 eV) (Fig. 4b).

Inclusions of Ca and N compounds (up to ca. 2 at. % and 1 at. %, respectively) were detected to be present in the oxide film, and the quantities of these elements also depended on the composition of oxide formation solution (Fig. 3b). The reduction in Ca concentration was determined at a 0.5–2.5 nm depth of oxide layer for the both steel oxidizing solutions, while the incorporation of N compounds in the oxide layer was found to be twice higher in the case when film formation took place in a solution containing Cl⁻.

The morphology and compactness of oxide films on steel surface were examined by means of AFM studies (Fig. 5). The presence of inhibitor Ca(NO$_2$)$_2$ in a saturated Ca(OH)$_2$ solution caused formation of a less porous and more compact oxide (Fig. 5b), while the surface of oxide layer formed in a blank solution possessed more structural defects and higher surface roughness (Fig. 5a). The root-mean-square roughness (R_{rms}) value of the latter sample was 9.78 nm, *versus* R_{rms} ~5.9 nm of the steel surface oxidized in solution with the inhibitor. The AFM and XPS results imply that calcium nitrite modified the oxide film on the steel bar to be more protective than the film formed in a solution without the inhibitor.

To summarize, Ca(NO$_2$)$_2$ ensured the most pronounced inhibition of steel corrosion in a saturated Ca(OH)$_2$ + 0.1 M NaCl solution. A passive layer formed on the metal surface in the mentioned solution was about 1.7 to 2.4 nm thick, contained N and was more compact and protective in comparison with oxide layers formed in media without the inhibitor. Ca(NO$_2$)$_2$ seems to strengthen the protective properties of the passive layer on steel and thus to increase the concentration of Cl⁻ at which passive corrosion turns into active or pitting corrosion.

Tests in concrete

The corrosion behaviour of steel in concrete structures with an inhibitor has been investigated by means of concrete cylinders tests in neutral salt spray and CO$_2$ chambers, as well as by cylinder immersion in 5% NaCl solution. Steel corrosion under salt spray conditions and in NaCl solution is induced by Cl⁻ ions, meanwhile in the CO$_2$ chamber the corrosion is effected by the reduction of the pH of the ambient because of the concrete carbonization process.
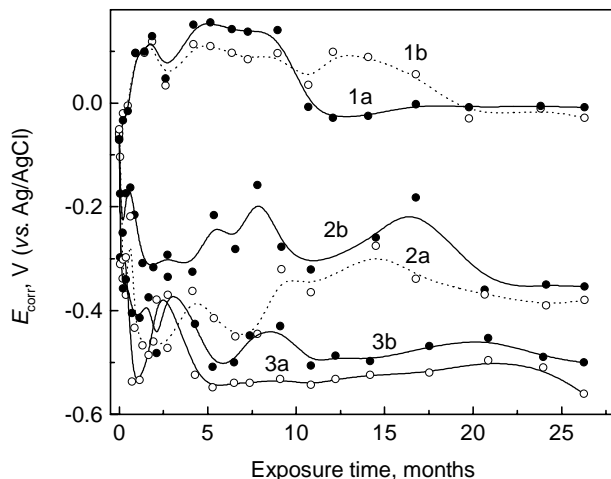

Fig. 5. AMF images of the steel surface after 1 hour exposure to a saturated Ca(OH)$_2$ solution without (*a*) and with (*b*) 0.05 M Ca(NO$_2$)$_2$

Fig. 6. Corrosion potential of reinforced concrete E_{corr} without (a) / with (b) $Ca(NO_2)_2$ exposed to: 1 – CO_2 chamber, 2 – 5% NaCl solution, 3 – NaCl chamber

The corrosion potentials of the steel rebar were monitored for 27 months, and the results are presented in Fig. 6. As one can see from the E_{corr}–τ plots, the samples exposed to the neutral salt spray chamber possessed the most negative potentials of steel reinforcement ($E_{corr} \sim -0.5 - -0.55$ V), meanwhile the samples exposed to the CO_2 chamber exhibited the most positive ones ($E_{corr} \sim 0 - -0.08$ V).

There are neither single corrosion potential values that uniformly define the limit between passive and active corrosion behaviour nor 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. A comparison of the E_{corr} values of samples with and without nitrite, exposed to a Cl⁻ containing ambient shows that in the presence of inhibitor the steel potentials are by up to 0.1 V more positive in respect to the samples without nitrite (Fig. 6), while for cylinders exposed to the CO_2 chamber (Fig. 6, curves 1a and 1b) whose ambient did not possess Cl⁻ ions, the potentials of steel were positive enough during the whole experiment, implying that no active corrosion of steel was initiated in the course of 27 months. It seems that the carbonization rate of concrete used for bridge construction is not high.

It has been known that cement itself has the ability to bind some chloride ions, as Friedel's salt ($Ca_2Al(OH)_6Cl \cdot 2H_2O$), rendering it ineffective as a catalyst for corrosion. Below 0.6–1 kg/m³ of chloride in concrete, the alkalinity of concrete is enough to minimize corrosion, although not to eliminate it [1]. In spite of the fact that there was no more than 0.1 kg/m³ Cl⁻ in the concrete structures (cylinders), it was enough to affect the corrosion behaviour and rate of steel reinforcement.
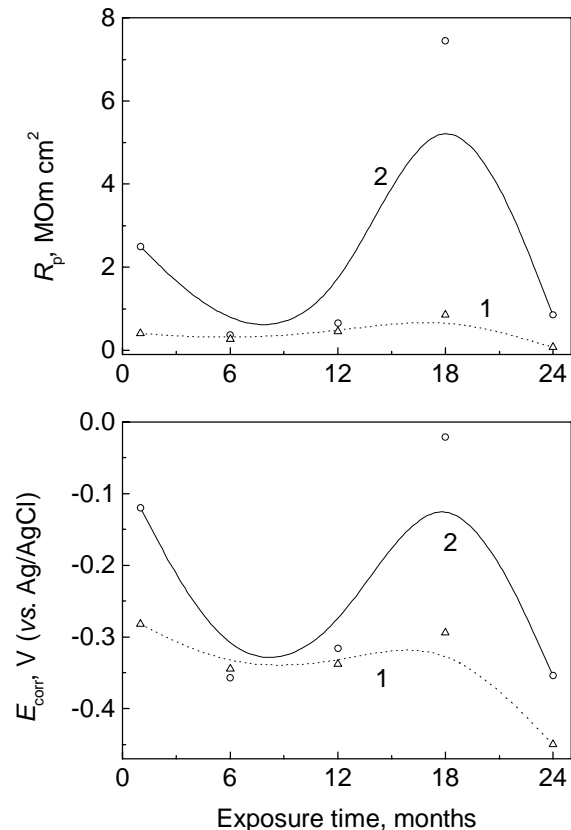

Fig. 7. Dependence of the corrosion potential E_{corr} (a) and the polarization resistance R_p (b) of reinforced concrete without (1) and with (2) $Ca(NO_2)_2$ on the time of exposure to 5% NaCl solution

EIS measurements were carried out with concrete cylinders immersed into 5% NaCl solution with the aim to determine the polarization resistance (R_p), which is in 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. 7a, together with the individual E_{corr} values of the same sample (Fig. 7b.). The experimental data were fitted assuming an equivalent circuit consisting of solution resistance and R_p in parallel with a constant phase element (CPE) [16] whose impedance is given by $Z_{CPE} = 1/C(j\omega)^{-n}$. The factor n was determined to be close to 1 (0.89–0.95). One can see that after a one month exposure of a concrete cylinder to a 5% NaCl solution the E_{corr} (Fig. 7b) values were by ca. 0.16 V more positive, while the corresponding R_p values (Fig. 7a) were six-fold higher for the sample containing the inhibitor versus the samples without it. Meanwhile, after six months of exposure the influence of the inhibitor on the E_{corr} and R_p values was not so evident. However, the beneficial effect of inhibitors manifests itself after more than a year of exposure; e.g., after one and a half year of exposure the potential of steel reinforcement was by 0.2–0.25 V more positive and the R_p values were up to 9 times higher was compared with

those obtained without the inhibitor in the concrete. Meanwhile, after two years of exposure the differences of E_{corr} and R_p for various samples were not so evident again. The fluctuations of R_p and E_{corr} values of a steel rebar in concrete are common phenomena for similar investigations and are related most probably with the repassivation process of corroded areas. In spite of the mentioned fluctuations, the inhibitory effect of nitrite on steel corrosion survives through the whole test period.

The obtained data show that introduction of nitrite into the concrete used for bridge construction or into alkaline chloride containing aqueous solutions reduce the corrosion rate of steel reinforcement.

CONCLUSIONS

According to the accelerated corrosion test, calcium nitrite is an effective inhibitor of steel corrosion in both investigated media: chloride containing alkaline solution and concrete used for bridge construction.

The inhibitory effect of nitrite on steel corrosion in alkaline media manifests through the improvement of protective properties of corrosion products (oxide films). The presence of chloride in corrosion media reduces the thickness of the oxide layer and influences its composition (Fe_2O_3, Fe_3O_4 with Cl^- and Fe_2O_3, FeOOH without Cl^-), while the presence of inhibitor yields formation of a less porous and more compact oxide film.

The most aggressive conditions (the most negative E_{corr} values) for steel rebar corrosion of concrete samples were observed in the accelerated test in a neutral salt spray chamber, while the concrete carbonization process (CO_2 chamber) did not initiate steel corrosion after two years of exposure.

References

1. M. Gaidis, *Cement & Concrete Composites*, **26**, 181 (2004).
2. G. Batis, N. Kouloumbi and P. Pantazopoulou, *Pigment & Resign Technology,* **29**, 159 (2000).
3. G. Batis, P. Pantazopoulou and A. Routoulas, *Anti-Corrosion Methods and Materials*, **48**, 107 (2001).
4. C. A. Loto, *Corrosion*, **48**, 759 (1992).
5. H. Saricimen, M. Mohammad, A. Quddus, M. Shameem and M. S. Barry, *Cement & Concrete Composites*, **24**, 89 (2002).
6. C. Monticelli, A. Frignani and G. Trabanelli, *Cement and Concrete Research*, **30**, 635 (2000).
7. N. S. Berke and M. C. Hicks, *Cement & Concrete Composites*, **26**, 191 (2004).
8. O. T. de Rincón, O. Pérez, E. Paredes, Y. Caldera, C. Urdaneta and I. Sandoval, *Cement & Concrete Composites*, **24**, 79 (2002).
9. W. D. Collins, R. E. Weyers and I. L. Al-Qadi, *Corrosion*, **49**, 74 (1993).
10. C. Monticelli, A. Frignani, G. Brunoro, G. Trabanelli, F. Zucchi and M. Tassinari, *Corrosion Science*, **35**, 1483 (1993).
11. J.-M. R. Génin, L. Dhouibi, Ph. Refait, M. Abdelmoula and E. Triki, *Corrosion*, **58**, 467 (2002).
12. H. Amar, J. Benzakour, A. Derja, D. Villemin and B. Moreau, *J. Electroanal. Chem.*, **558**, 131 (2003).
13. N. Nakayama, *Corrosion Science*, **42**, 1897 (2000).
14. N. Nakayama and A. Obuchi, *Corrosion Science*, **45**, 2075 (2003).
15. H. E. Jamil, A. Shriri, R. Boulif, C. Bastos, M. F. Montemor and M. G. S. Ferreira, *Electrochim. Acta*, **49**, 2753 (2004).
16. E. Juzeliûnas, K. Leinartas, M. Samulevièienë, P. Mièèinskas, R. Juðkënas and A. Sudavièius, *Corrosion Science*, **44**, 1541 (2002).
17. O. Girèienë, M. Samulevièienë, A. Sudavièius and R. Ramanauskas, *Bulletin of Electrochemistry* (submitted).

Olga Girèienë, Meilutë Samulevièienë, Aloyzas Sudavièius, Rimantas Ramanauskas, Leontij Lapuchin

PLIENO KOROZIJOS INHIBITORIAUS KALCIO NITRITO VEIKSMINGUMAS ŠARMINIUOSE TIRPALUOSE IR BETONE

S a n t r a u k a

Plieno korozija tirta sotaus $Ca(OH)_2$ + 0,1 M NaCl su/be inhibitoriumi $Ca(NO_2)_2$ tirpaluose bei gelþbetoniniuose pavyzdþiuose, pagamintuose ið betono, naudojamo tiltø statyboje. Gelþbetoniniø pavyzdþiø pagreitinti koroziniai tyrimai atlikti patalpinus juos á 5% NaCl tirpalà, druskos rûko bei CO_2 kameras. Atviros grandinës potencialo matavimai ir EIS (elektrocheminio impedanso spektroskopijos metodas) naudoti korozijos procesui apibûdinti, XPS – korozijos produktø analizei, AFM – pavirðiaus morfologiniams tyrimams. Atlikti tyrimai parodë, kad pasyvi oksidinë plëvelë, susiformuojanti ant plieno pavirðiuje ðarminiame tirpale su kalcio nitritu, yra kompaktiðkesnë ir tvirtesnë, palyginus su gautàja ið tirpalo be inhibitoriaus.