
Evaluation of the efficiency of the secondary corrosion protection of steel reinforcement bars in concrete using a bimetallic batch sensor

D.S. Shevtsov,[1] N.L. Cao,[2]* I.D. Zartsyn,[1] V.C. Nguyen,[2] Q.Q. Nong,[2] H.Q. Le,[2] D.A. Nguyen,[2] E.S. Komarova,[1] D.A. Zhikhareva,[1] O.A. Kozaderov[1] and A.T. Nguyen[3]

[1] *Faculty of Chemistry, Voronezh State University, Universitetskaya pl. 1, 394018 Voronezh, Russian Federation*
[2] *Coastal Branch, the Joint Vietnam-Russia Tropical Science and Technology Research Center, Nguyen Thien Thuat St., 30, Nha Trang, Khanh Hoa, 57127, Vietnam*
[3] *Faculty of Chemistry, Ho Chi Minh City University of Education, An Duong Vuong St., 280, Ho Chi Minh, 700000, Vietnam*
**E-mail: cnlinh0812@vrtc.org.vn*

Abstract

Bimetallic batch sensors allow evaluating the protective effect of compositions used for the secondary corrosion protection of reinforced concrete. Such compositions significantly reduce the permeability of concrete due to hydrophobization of the capillary pore structure. This conclusion was drawn from the fact that there is a good agreement with the measurement results obtained with the help of standardized electrochemical methods (specific electrical resistance of concrete, free corrosion potential, and the rate of corrosion calculated using the LPR data). A set of non-destructive electrochemical methods for corrosion testing was used to show the efficiency of the secondary protection of reinforced concrete against destruction of steel reinforcement bars by applying MasterProtect 8500 CI, a commercial product, to samples of mortar in the laboratory. According to qualitative criteria, the protective effect was at least 24 times higher as compared to untreated control samples. The corrosion rate was reduced by 100–200 times. It was suggested that there is a double protection mechanism due to the increased specific electrical resistance of concrete (hydrophobization of the surface of capillaries) and inhibition of electrochemical corrosion.

Received: August 16, 2022. Published: August 19, 2022 doi: 10.17675/2305-6894-2022-11-3-19

Keywords: *bimetallic batch sensor, free corrosion potential, specific electrical resistance of concrete, LPR, hydrophobizator.*

1. Introduction

Evaluation of the efficiency of the primary (concrete additives) and secondary (impregnation, coatings, migrating corrosion inhibitors) corrosion protection of reinforced concrete is still very important. The results of new developments have been presented in hundreds of scientific publications proposing new substances and compositions to prevent corrosion of steel reinforcement bars in concrete [1–3]. These compositions have varying degrees of efficiency and have been tested in laboratories [4, 5] or in the field [6, 7]. Additionally, major and regional manufacturers of construction chemicals have extensive product lines of commercial off-the-shelf products used to increase the protective properties of concrete, including corrosion protection of steel reinforcement bars. For the end user, especially when designing crucial infrastructure facilities, technical specifications are often not helpful enough to determine which of the proposed materials is the most effective or has the best price-quality ratio. In such cases, accelerated tests simulating impacts expected during the operation of the facilities are required.

Currently, the most developed and justified in terms of regulatory documents are the following non-destructive methods for evaluating the corrosion behavior of steel reinforcement bars in concrete: the qualitative methods of measuring the specific electrical resistance of concrete [8, 9] and the free corrosion potential (half-cell potential) [10, 11] and the quantitative method of linear polarization resistivity [12, 13]. Among new developments are various sensor systems that are considered promising for field applications, especially for remote monitoring. The most common include galvanic cell [14], fiber-optic [15], and acoustic [16] sensors. The advantage of many sensors and sensor-based systems is the possibility to collect data remotely using relatively simple instruments (for example, a microammeter for galvanic cells). Typically, the adequacy of their application is compared with the standardized methods described above. It should be noted that the application of such systems is usually considered in the context of detecting the onset of corrosion or predicting the destruction intensity under the action of chlorides or carbon dioxide. However, they are less frequently used to evaluate the efficiency of the primary and secondary protection of reinforced concrete.

The purpose of the work is to test bimetallic batch sensors (BBS) of an original design used as devices to evaluate the efficiency of the secondary corrosion protection of reinforced concrete (increasing the time before the onset of corrosion and reducing the rate of corrosion). Such corrosion protection significantly reduces the permeability of concrete due to hydrophobization under the periodic action of chlorides. The secondary protection used during the study was MasterProtect 8500 CI, a commercial product.

2. Experimental

To simulate the corrosion process of steel reinforcement bars in concrete, we used BBS (Figure 1) proposed in [17].

The sensors were installed in 160×130×40 mm mortar prisms so that the layer thickness above the working metal surface was 20 mm. Two steel reinforcement bars with a diameter of 6 mm were placed parallel to the sensor (Figure 2). The composition of the steel reinforcement bars is shown in Table 1.

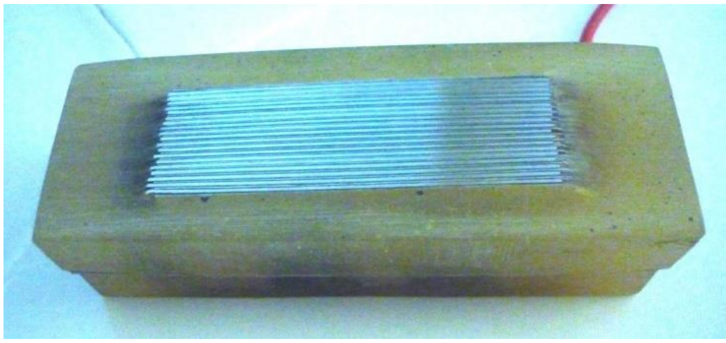


Figure 1. Bimetallic batch sensor.

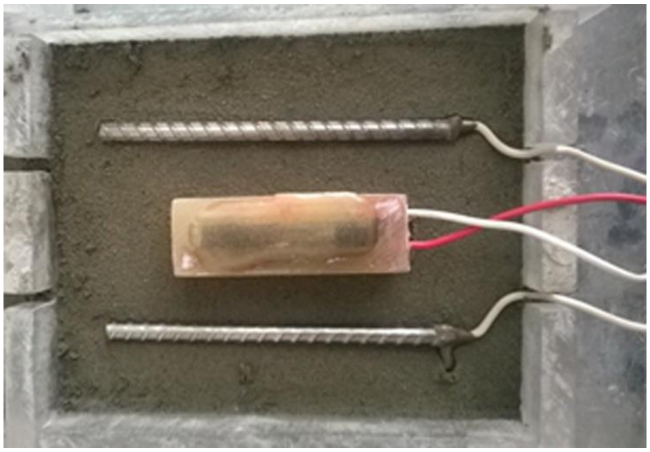


Figure 2. A sample of mortar at the manufacturing stage.

Table 1. Chemical composition of steel reinforcement bars.

Main components	Mass fraction of the components, %
Fe	93.637
C	0.24
Si	0.95
Mn	1.70
P	0.055
S	0.055
N	0.013
Cu	0.35

The cement–sand mortar mixture was prepared using M500 cement (according to the GOST standard 10178-85 – Ordinary Portland cement (Tables 2,3)). The water-cement ratio (w/c) was 0.45 wt.%; the mass ratio of cement and sand was 1:3. The samples were cured for 28 days at 100% humidity and were extracted from the formwork after 7 days.

Table 2. Chemical composition of cement.

Main components	Mass fraction of the components, %
CaO	64.56±0.4
SiO_2	20.99±0.2
Al_2O_3	5.26±0.07
Fe_2O_3	3.91±0.04
MgO	0.83±0.01
SO_3	1.14±0.01
Alkaline oxides in terms of Na_2O	0.9±0.02
Other	2.41±0.03

Table 3. Phase composition of cement.

Main phases	Mass fraction of the phases, %
C_3S	60.3±0.6
C_2S	13.2±0.5
C_3A	7.3±0.5
C_4AF	11.9±0.1
Other	7.3±0.3

The concrete surface was treated with MasterProtect 8500 CI, commercially produced hydrophobizator-migrating corrosion inhibitor based on silanes and a mixture of organic inhibitors, including aminoalcohols, as described in the product details. (The exact composition is a trade secret). The consumption was $0.6\ dm^3 \cdot m^{-2}$. The experiment started two weeks after the treatment.

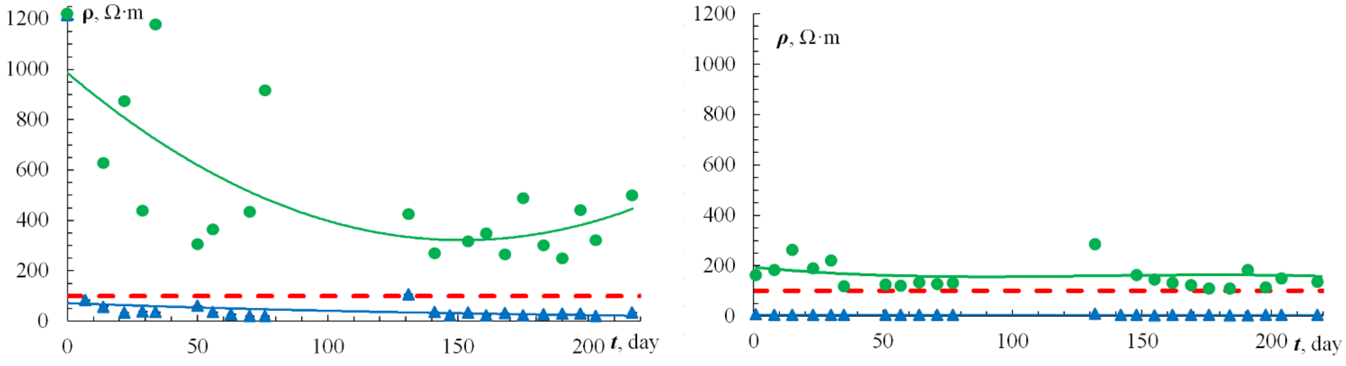
During the experiment, the mortar samples were immersed in a 3% NaCl aqueous solution for 1 day. They were then transferred to a laboratory atmosphere with a natural relative humidity of 35±5% and a temperature of 22±2°C, where they were dried for six days.

The electrical resistance of the mortar (ρ) was measured using the four-electrode Wenner method on the surface of the mortar according to AASHTO T358-19 [18]. At the same time, in accordance with ASTM C876-15 [19], free corrosion potentials (E_{cor}) of steel under the layer of mortar on the surface were monitored. The values of electrode potentials are shown on the scale of the copper-sulfate reference electrode (the offset with respect to the scale of the standard hydrogen electrode is +0.318 V). Corrosion current density (i_{cor}) was estimated by the method of linear polarization resistance in accordance with RILEM recommendations [20]. The value of current density i_{cor} was calculated in relation to the visible area of the steel reinforcement bar. Current sensor measurements within the sensor were carried out using a zero-resistance ammeter [21]. The current density within the sensor was calculated in relation to the visible area of steel plates. The measurements of the above parameters were carried out for dry and moisture-saturated conditions.

3. Results and discussion

The specific electrical resistance of the mortar after hydrophobization significantly increased in comparison with the control composition (Figure 3). For dry control samples, after the first immersion in the chloride solution and until the end of the experiment, the values of ρ were in the range from 19 to 100 Ω·m. For the moisture-saturated samples, ρ varied in the range from 4 to 9 Ω·m. All obtained values corresponded to a high corrosion risk according to the criteria [18]. For dry samples, immediately after hydrophobization, ρ was from 600 to 1200 Ω·m. Then there was a slight decrease to 250–500 Ω·m. For the chloride-saturated samples, ρ was from 110 to 290 Ω·m. The results for dry hydrophobized mortar corresponded to a low or insignificant risk of corrosion, while for the saturated mortar the risk was moderate.

Treatment with MasterProtect 8500 CI significantly, by 15–55 times, increased the specific electrical resistance of the mortar. This effect is probably associated with the formation of a hydrophobic film on the surface of the pores within the capillary pore system of the mortar. The effect was maintained for at least 24 cycles of immersion in a 3% NaCl solution.

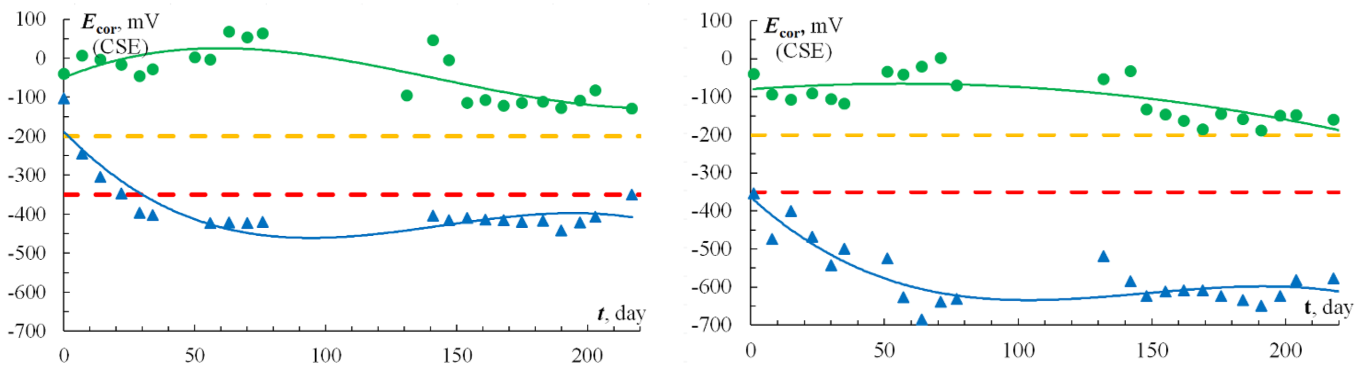


a b

Figure 3. The change in specific electrical resistance (ρ) of the mortar during cycles of immersion in a 3% NaCl solution for dry (a) and saturated (b) samples: ▲ – control, ● – after hydrophobization.

The free corrosion potential of steel reinforcement bars within dry samples without hydrophobization decreased gradually during the experiment (Figure 4a). The initial values of E_{cor} were at the boundary of the passive and uncertain corrosion state according to [19]. After the fourth immersion, even for dry samples, the measured E_{cor} unambiguously indicated a transition to active corrosion. For the solution-saturated samples, the transition to corrosion already occurred after the first immersion (Figure 4b). For dry and moisture-saturated hydrophobized samples, the measured values corresponded to the passive state during 24 immersion cycles. What is more, there was a gradual decrease in E_{cor} over time.

According to the qualitative criterion of the free corrosion potential, the treatment with MasterProtect 8500 CI increased the time before the onset of corrosion at least by 24 times as compared to the control samples.



a b

Figure 4. The change in free corrosion potential of the reinforcement bars in the mortar (E_{cor}) during cycles of immersion in a 3% NaCl solution for dry (a) and saturated (b) samples: ▲ – control, ● – after hydrophobization.

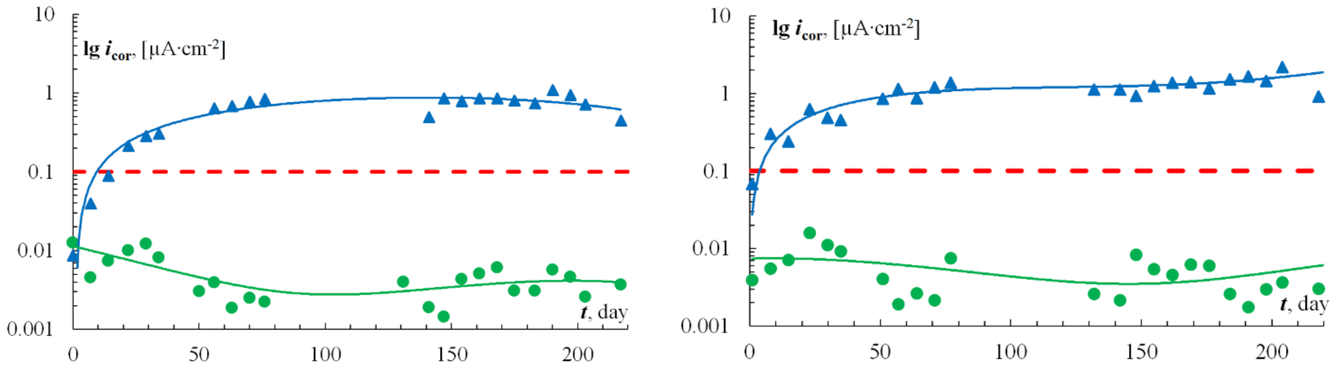
The estimated values of the corrosion current density calculated using the LPR data changed in accordance with E_{cor}. For dry samples, the transition to the corrosion of the reinforcement bars in the mortar without hydrophobization with an excess of 0.1 $\mu\text{A}\cdot\text{cm}^{-2}$ [20] was obtained by the fourth immersion in the chloride solution (Figure 5a). Within 10–12 cycles, there was a linear increase in i_{cor}. Then, the maximum value was reached in the range of 0.8–1.1 $\mu\text{A}\cdot\text{cm}^{-2}$. This corresponds to a moderate rate of corrosion. For the saturated samples, the transition to corrosion was noted by the second immersion.

With an increase in the number of immersions, there remained a gradual increase in i_{cor} up to 2.2 $\mu\text{A}\cdot\text{cm}^{-2}$. For samples after hydrophobization, all calculated i_{cor} values were below the threshold value, on average, by 10 times (Figure 5b).

According to the quantitative criterion of the corrosion current density, the treatment with MasterProtect 8500 CI increased the time before the onset of corrosion at least by 24 times as compared to the control samples. The difference between the calculated values of i_{cor} for steel reinforcement bars in the control mortar and the samples after hydrophobization exceeded 100–200 times.

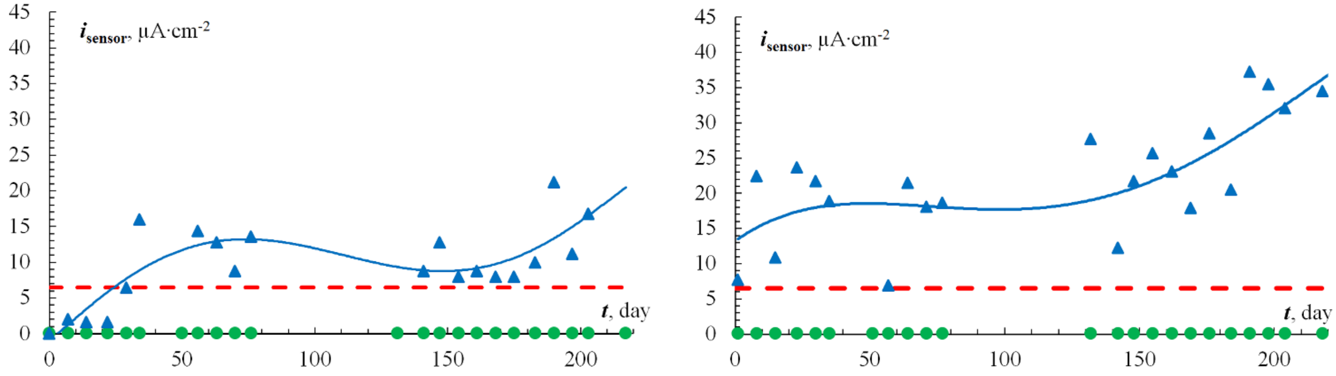
The obtained correspondence between qualitative (ρ, E_{cor}) and quantitative (i_{cor}) criteria for evaluating corrosion of steel reinforcement bars in the mortar under local activation by the periodic action of chlorides agrees well with previously obtained results [22, 23].

The current density at BBS for dry control samples exceeded the threshold value of 6.5 $\mu\text{A}\cdot\text{cm}^{-2}$ [24] after four immersions in the chloride solution (Figure 6a). After that, the measured values were from 8.8 to 22 μA·cm^{-2}. For moisture-saturated mortar, after the first immersion, there was a transition to corrosion with a gradual increase in i_{sensor} to 34–37 μA·cm^{-2} by the 24th immersion cycle. For dry and moisture-saturated samples after hydrophobization, throughout the experiment, the i_{sensor} was not measured within the ammeter accuracy of 0.5 μA·cm^{-2} (Figure 6b).



a b

Figure 5. The change in corrosion current density of the reinforcement bars in the mortar (i_{cor}) during cycles of immersion in a 3% NaCl solution for dry (a) and saturated (b) samples: ▲ – control, ● – after hydrophobization.



a b

Figure 6. The change in the current within the BBS in the mortar (i_{sensor}) during cycles of immersion in a 3% NaCl solution for dry (a) and saturated (b) samples: ▲ – control, ● – after hydrophobization.

Thus, it was shown that BBS can be used as a system for evaluating the efficiency of the secondary corrosion protection of reinforced concrete which changes the specific electrical resistance of concrete and acts as a corrosion inhibitor. Taking into account that the data were collected by simple instruments (a zero-resistance microammeter), the BBS-based system of corrosion monitoring of steel reinforcement bars can be used not only for "ordinary" reinforced concrete structures, as was shown earlier [21], but also for the secondary protection with hydrophobizators.

The results obtained for the evaluation of the efficiency of the MasterProtect 8500 CI secondary protection are intermediate and the study will continue until the onset of corrosion process is established and/or the control samples are significantly destroyed.

4. Conclusion

When evaluating the efficiency of the secondary corrosion protection of reinforced concrete using the example of a commercially available hydrophobizator-migrating corrosion inhibitor, a correspondence was established between the existing methods of evaluating the corrosion behavior embodied in standards and regulations (specific electrical resistance, free corrosion potential, and corrosion current) and the readings of the bimetallic batch sensor designed as proposed in the article.

It was found that the protective action of MasterProtect 8500 CI for the secondary protection of reinforced concrete with regard to steel reinforcement bars is associated with both an increase in the specific electrical resistance (due to a decrease in permeability) of the mortar and with the inhibition of the electrochemical process of steel oxidation.

It was found that the time before the onset of steel reinforcement corrosion after the mortar had been treated with MasterProtect 8500 CI increased by at least 24 times in comparison with the control samples. What is more, a decrease in the rate of corrosion calculated using the LPR data was by 100–200 times.

Acknowledgements

This research was funded by the Joint Vietnam-Russia Tropical Science and Technology Research Center (project number 931/QĐ-TTNĐVN).

References

1. F. Bolzoni, A. Brenna and M. Ormellese, Recent advances in the use of inhibitors to prevent chloride-induced corrosion in reinforced concrete, *Cem. Concr. Res.*, 2022, **154**, 106719. doi: 10.1016/j.cemconres.2022.106719
2. C. Venkatesh, S.K. Mohiddin and N. Ruben, Corrosion inhibitors behaviour on reinforced concrete – a review, *Sustainable Constr. Build. Mater.*, 2019, 127–134. doi: 10.1007/978-981-13-3317-0_11
3. A. Goyal, H.S. Pouya, E. Ganjian and P. Claisse, A review of corrosion and protection of steel in concrete, *Arabian J. Sci. Eng.*, 2018, **43**, no. 10, 5035–5055. doi: 10.1007/s13369-018-3303-2
4. I.A. Gedvillo, A.S. Zhmakina, N.N. Andreev and S.S. Vesely, Protection of rusted reinforcing steel in concrete by IFKhAN-85 inhibitor, *Int. J. Corros. Scale Inhib.*, 2020, **9**, no. 2, 562–570. doi: 10.17675/2305-6894-2020-9-2-11

---

5. R. Anitha, S. Chitra, V. Hemapriya, I.M. Chung, S.H. Kim and M. Prabakaran, Implications of eco-addition inhibitor to mitigate corrosion in reinforced steel embedded in concrete, *Constr. Build. Mater.*, 2019, **213**, 246–256. doi: 10.1016/j.conbuildmat.2019.04.046
6. A. Abd El Fattah, I. Al-Duais, K. Riding and M. Thomas, Field evaluation of corrosion mitigation on reinforced concrete in marine exposure conditions, *Constr. Build. Mater.*, 2018, **165**, 663–674. doi: 10.1016/j.conbuildmat.2018.01.077
7. S.N. Leonovich, L.S. Karpushenkava and S.A. Karpushenkov, Migrating Corrosion Inhibitor (MCI) for Concrete Rebar and Its Inhibitory Efficiency, *Adv. Constr. Dev.*, 2022, 195–203. doi: 10.1007/978-981-16-6593-6_21
8. K. Hornbostel, C.K. Larsen and M.R. Geiker, Relationship between concrete resistivity and corrosion rate – A literature review, *Cem. Concr. Compos.*, 2013, **39**, 60–72. doi: 10.1016/j.cemconcomp.2013.03.019
9. K.P.V. Robles, J.J. Yee and S.H. Kee, Electrical Resistivity Measurements for Nondestructive Evaluation of Chloride-Induced Deterioration of Reinforced Concrete – A Review, *Materials*, 2022, **15**, no. 8, 2725. doi: 10.3390/ma15082725
10. B. Elsener, C. Andrade, J. Gulikers, R. Polder and M. Raupach, Half-cell potential measurements – Potential mapping on reinforced concrete structures, *Mater. Struct.*, 2003, **36**, no. 7, 461–471. doi: 10.1007/BF02481526
11. Z.H. Zou, J. Wu, Z. Wang and Z. Wang, Relationship between half-cell potential and corrosion level of rebar in concrete, *Corros. Eng., Sci. Technol.*, 2016, **51**, no. 8, 588–595. doi: 10.1080/1478422X.2016.1167304
12. G. Song, Theoretical analysis of the measurement of polarisation resistance in reinforced concrete, *Cem. Concr. Compos.*, 2000, **22**, no. 6, 407–415. doi: 10.1016/S0958-9465(00)00040-8
13. J.E. Ramón, A. Castillo and I. Martínez, On-site corrosion monitoring experience in concrete structures: potential improvements on the current-controlled polarization resistance method, *Mater. Constr. (Madrid, Spain)*, 2021, **71**, no. 344, 265.
14. R.B. Figueira, Electrochemical sensors for monitoring the corrosion conditions of reinforced concrete structures: A review, *Appl. Sci.*, 2017, **7**, no. 11, 1157. doi: 10.3390/app7111157
15. L. Fan and Y. Bao, Review of fiber optic sensors for corrosion monitoring in reinforced concrete, *Cem. Concr. Compos.*, 2021, **120**, 104029. doi: 10.1016/j.cemconcomp.2021.104029
16. Y. Yu, A. Safari, X. Niu, B. Drinkwater and K.V. Horoshenkov, Acoustic and ultrasonic techniques for defect detection and condition monitoring in water and sewerage pipes: A review, *App. Acoust.*, 2021, **183**, 108282. doi: 10.1016/j.apacoust.2021.108282

17. D.S. Shevtsov and I.D. Zartsyn, Evaluation of the effectiveness of migrating corrosion inhibitors and hydrophobizers for protection against corrosion of steel reinforcement in concrete using bimetallic batch sensor, *Int. J. Corros. Scale Inhib.*, 2018, **7**, no. 3, 427–442. doi: 10.17675/2305-6894-2018-7-3-12
18. AASHTO American Association of State Highway and Transportation Officials T358, Standard Method of Test for Surface Resistivity Indication of Concrete's Ability to Resist Chloride Ion Penetration, 2019.
19. ASTM C876-15, Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete, ASTM International, West Conshohocken, PA., 2015. doi: 10.1520/C0876-15
20. C. Andrade and C. Alonso, Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method, *Mater. Struct.*, 2004, **37**, no. 9, 623–643. doi: 10.1007/BF02483292
21. D.S. Shevtsov, I.D. Zartsyn and E.S. Komarova, System for Continuous Monitoring of the Corrosion Rate in Concrete Reinforcement based on Bimetallic Batch Sensors, *Prot. Met. Phys. Chem. Surf.*, 2021, **57**, no. 7, 1388–1394. doi: 10.1134/S2070205121070182
22. D.L. Caudill and R.P. Guisinger, A Comparison Of Astm C 876 Potential Criteria And Linear Polarization Resistance Measurements On A 70,000 Ft2 (6,503 M2) Reinforced Concrete Bus Ramp, *Corrosion 97*, 1997.
23. S. Choudhary, A. Garg and K. Mondal, Relation between open circuit potential and polarization resistance with rust and corrosion monitoring of mild steel, *J. Mater. Eng. Perform.*, 2016, **25**, no. 7, 2969–2976. doi: 10.1007/s11665-016-2112-6
24. I.D. Zartsyn and D.S. Shevtsov, Simulation of electrochemical corrosion of steel reinforcement in reinforced concrete structures with use of bimetal packet-type sensor, *Korroz.: Mater., Zashch. (Corrosion: materials, protection)*, 2018, no. 2, 31–40 (in Russian).

◆ ◆ ◆