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# Development of method for assessing efficiency of organic corrosion inhibitors in concrete reinforcement

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Preliminary note

**Ivana Šoić, Sanja Martinez, Ivana Lipošćak, Boris Mikšić**

## Development of method for assessing efficiency of organic corrosion inhibitors in concrete reinforcement

The applicability of electrochemical impedance spectroscopy in a cell consisting of a steel plate covered with concrete layer containing chlorides and inhibitor, constructed in accordance with HRN EN ISO 16773, is studied for the first time in this paper. The measurements have enabled quantification of harmful chloride action and inhibitor efficiency, understanding the mechanism and time dependence of inhibitory activity, and visual inspection of metal surface after measurement. The results are consistent with the presumed physical model and point to the applicability of the method.

### Key words:

corrosion, reinforcement, concrete, EIS, migrating inhibitor, chlorides, efficiency

Prethodno priopćenje

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## Razvoj metode za određivanje djelotvornosti organskih inhibitora korozije armature u betonu

U radu se prvi put ispituje primjenjivost elektrokemijske impedancijske spektroskopije (EIS) u čeliji s čeličnom pločom prekrivenom slojem betona s dodatkom klorida i inhibitora, konstruiranoj u skladu s normom HRN EN ISO 16773. Mjerenje je omogućilo kvantificiranje štetnog utjecaja klorida i zaštitne djelotvornosti inhibitora, razumijevanje mehanizma i praćenje vremenske ovisnosti inhibitorskog djelovanja, te vizualni pregled površine metala nakon mjerenja. Rezultati su usklađeni sa zamišljenom fizikalnom slikom i upućuju na primjenjivost metode.

### Ključne riječi:

korozija, armatura, beton, EIS, migrirajući inhibitor, kloridi, djelotvornost

Vorherige Mitteilung

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## Entwicklung einer Methode zur Bestimmung der Wirksamkeit von organischen Korrosionshemmstoffen für Betonbewehrung

In der Abhandlung untersucht man zum ersten Mal die Anwendbarkeit der elektrochemischen Impedanzspektroskopie (EIS) in einer Zelle mit einer Stahlplatte, die mit einer Betonschicht mit Zusatz von Chlorid und einem Hemmstoff bedeckt ist, konstruiert in Übereinstimmung mit der Norm HRN EN ISO 16773. Die Messung ermöglichte die Quantifizierung des schädlichen Einflusses von Chlorid und der schützenden Wirksamkeit des Hemmstoffs, das Verständnis des Mechanismus und die Überwachung der zeitlichen Abhängigkeit der Wirksamkeit des Hemmstoffs sowie eine visuelle Überprüfung der Metalloberfläche nach der Messung. Die Ergebnisse stimmen mit dem erdachten physikalischen Bild überein und weisen auf die Anwendbarkeit der Methode hin.

### Schlüsselwörter:

Korrosion, Bewehrung, Beton, EIS, Migrationsinhibitor, Chloride, Wirksamkeit

## 1. Introduction

The corrosion of reinforcement steel is the most common cause of premature deterioration and shortening of the lifetime of reinforced concrete structures [1]. Under normal operating conditions, concrete is not an aggressive corrosion environment for steel. Steel corrosion in concrete occurs if concrete is not of a suitable quality, if structure is not properly designed for aggressive exposure, if the environment is more aggressive than provided for in structural design, or if it changes during the lifetime of the structure.

Built-in steel is fully protected in new concrete structures; the pH of the pore water is high and there is only a small amount of chloride in the concrete if chlorinated contaminants are not used [2]. According to HRN EN 206: 2016 [3], the maximum permissible chloride content is 0.4 % relative to the cement mass. Regardless of the starting state, after a certain time the conditions in concrete may become suitable for corrosion. The concrete barrier layer is not perfect because of its porous structure and existing micro cracks that allow penetration of aggressive substances, which then cause the passive layer to fall on the reinforcement [4].

The volume of corrosion products is four to six times greater than the volume of steel from which the products were produced. This increase in volume causes tensile stresses in concrete, and when these stresses exceed the permitted tensile strength of concrete, the protective layer is damaged by cracking, crushing, or bending. Apart from the loss of the protective layer, the reinforced concrete structure can be damaged due to cross-sectional reduction of steel and the loss of concrete and steel connection. Chloride-induced corrosion of reinforcing steel is the major cause of corrosion in concrete around the world and requires great investment in maintenance or renovation [1, 5].

Corrosion inhibitors have been successfully used in the oil and process industry for years [6]. Their use as concrete additives is less widespread, although corrosion inhibitors are one of the most effective and simplest methods for corrosion control in reinforced concrete structures. Unlike techniques aimed at preventing penetration of aggressive substances into concrete, or keeping reinforcement away from corrosive environment when constructing a structure, inhibitors can provide corrosion protection both in new and existing structures, when aggressive substances are already present or even when corrosive process has already begun. The application of corrosion inhibitors in concrete is specified in HRN EN 1504-9 [7], as a method of protection No. 11.3. Among protective techniques mentioned in this standard, inhibitors stand out as a protection method because they directly affect the corrosion process [2]. The standard anticipates two modes of application of the inhibitor, by mixing in concrete, or by subsequent application on concrete surface. Subsequent application activates migratory amino acid-based (amino-alcohols and aminocarboxylates) corrosion-inhibiting (MCI®) inhibitors, which rapidly propagate by capillary forces and migrate through concrete structure to the metal surface [8, 9]. Other parts of HRN EN 1504 provide description and acceptable values for properties

of specific products and systems for the protection and repair of concrete structures. It is explicitly stated in HRN EN 1504-9 that there is no appropriate standard of the said series that relates to the use of a concrete inhibitor, and so the efficacy of the inhibitor should be determined before specifying its application. Therefore, it is of utmost importance to develop a reliable method for testing the inhibitory efficacy of concrete.

Designing and planning the maintenance and renovation of concrete structures require quality control and reliable techniques that can be used to determine the effectiveness and harmlessness of the proposed measures for the protection of concrete from degradation [5]. The only standardized method used to test the effectiveness of corrosion inhibitors in concrete is ASTM-G109 [10]. It is based on measuring corrosion potential and macrocell current. It requires long-term exposure and does not provide numerical value of inhibitory efficacy. In this paper, the construction of the electrochemical cell and the method of electrochemical impedance spectroscopy (EIS), described in a series of standards HRN EN ISO 16773-1 to 4 [11-14], are used for the first time to evaluate efficacy of corrosion inhibitors in concrete. These standards, issued in 2016 and 2017, were originally developed to measure protective properties of high-resistance organic coatings ( $> 10^9 \Omega \text{ cm}^2$ ), but the scope of their application was extended in the latest 2016 edition to samples with low resistance coatings and unprotected metallic samples. Among the advantages of the EIS method, it is important to emphasize the use of a very small amplitude AC voltage, which causes small current flows without destroying the examined metal surface, and the possibility of characterizing electrical properties and surface of the metal, as well as the layer of concrete on that surface [15]. Due to non-destructiveness of EIS, measurements can be repeated over time, and it is possible to keep track of corrosive behaviour of steel caused by corrosion properties of concrete itself, by penetration of aggressive substances into concrete, and by the admixing or migration of corrosion inhibitors into concrete. In this way, it is possible to simulate different situations that occur in practice, and to significantly reduce the time of the experiment.

This paper investigates the efficacy of three types of organic corrosion inhibitors mixed with concrete together with chlorides. The aim of the paper is to develop a new method to prove the efficacy of corrosion inhibitors and to help understand the inhibition of corrosion of reinforcement through time tracking of changes within the concrete itself and at the steel-concrete interface induced by the use of inhibitors.

## 2. Experimental

The samples were prepared using carbon steel Q-PANELS 0,02 x 2 x 3,5" as working electrodes, which simulated the reinforcement inside the concrete. Glass cylinders were used as a mould for the prepared mortar, and they were fixed to the steel surface using Poly Max® Original Express, a universal waterproof adhesive. The photo and the schematic representation of the cell are shown in Figures 1.a and 1.b.

Table 1. Sample composition

Sample	Water	Sand	Cement	1 % sodium chloride	Inhibitor
C	+	+	+	-	-
C+NaCl	+	+	+	+	-
INH A	+	+	+	+	+
INH B	+	+	+	+	+
INH C	+	+	+	+	+

The mortar was prepared according to HRN EN 196-3: 2009 - procedure 2 [16], using Portland cement, aggregate up to 4 mm in size, and water. Three samples of each composition were prepared (Table 1).

Organic migrating corrosion inhibitors used in the experiment, hereinafter referred to as INH A, B and C, contain a combination of amino-alcoholic salts of water-based carboxylic acids, whose primary purpose is to protect concrete steel from corrosion [8]. When admixed in concrete, they migrate to the reinforcement surface where they form a monomolecular layer that inhibits the corrosion reaction on the anode and cathode surfaces of the corrosion cell. Examined inhibitors are harmless to the environment and do not require safe handling measures. Because of its properties, the INH C inhibitor can cause longer hardening time of concrete, while INH A and INH B inhibitors do not affect the curing time and are often used in repair mortar. Mortar samples were prepared using the water/cement ratio of 0.5. A higher water/cement ratio is used to prepare highly-porous mortar to ensure that the corrosion begins during the experiment time and, more importantly, to determine if the protective agents used actually protect against those parts of the structure where there is such a high water/cement ratio. The mortar is used instead of concrete because the surface of the studied steel is not sufficient to allow the use of aggregates fractions larger than 4 mm [17]. After the preparation, the nurturing of the samples lasted for 7 days. After that, edges between the mortar and glass were sealed with Poly Max® Original Express to avoid faults due to electrolyte penetration between the two materials.

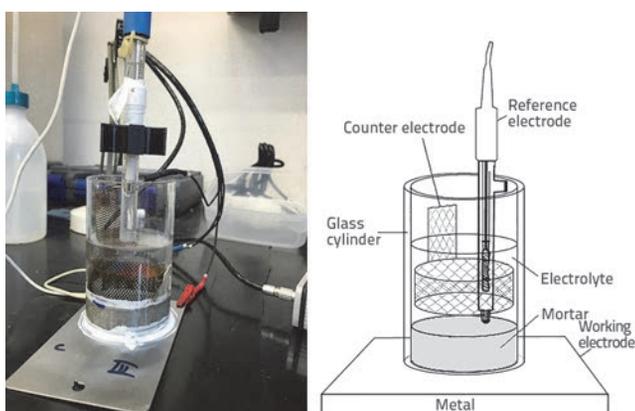


Figure 1. Picture and schematic representation of electrochemical working cell

Samples were cured for additional 7 days, after which 100 mL of saturated calcium hydroxide with 1 % NaCl were added to each cell. Samples were covered with transparent foil to prevent electrolyte evaporation in the period between measurements. The measurement was performed over 76 days, after 6, 23, 33, 54 and 76 days.

## 2.1. Electrochemical measurements

Electrochemical impedance spectroscopy measurements were carried out by means of a three-electrode system comprising previously described work electrode, a stainless steel mesh as a counter electrode, and a SCHOTT B3510 + calomel reference electrode, using a PalmSens 3 device with PStace software. The electrolyte was a saturated solution of calcium hydroxide with the addition of 1 % sodium chloride.

The corrosion potential was read immediately before the EIS measurement. EIS measurements were conducted in the frequency range between 50 kHz and 10 mHz. Sinusoidal voltage of  $\pm 50$  mV was supplied, and direct current (DC) potential was set to the corrosion potential.

## 3. Results and discussion

### 3.1. Electrochemical impedance spectroscopy

All impedance spectra were interpreted using equivalent circuits shown in Figure 2, which are considered suitable for reinforcement in concrete and mortar [17].

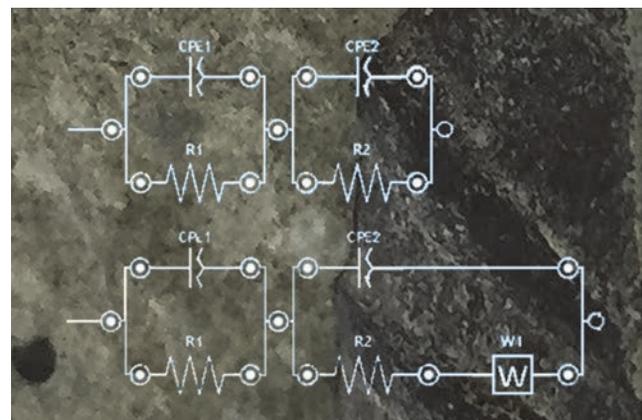


Figure 2. Electrochemical equivalent circuits used for impedance measurement

The proposed equivalent electric circuit is made of two serially-connected circuits consisting of a constant-phase element (CPE) and a resistor (R) in parallel connection. The first high-frequency parallel circuit can be attributed to dielectric properties of concrete [18], while the second low-frequency parallel circuit attributes to the steel/concrete interface. A part of the result is interpreted with an equivalent electric circuit that, besides the above mentioned, also contains a Warburg element, which represents a diffusion effect on the reaction of oxygen reduction that is running at sufficient speed to be under diffusion control, indicating active corrosion [19].

In the case of the upper equivalent circuit shown in Figure 2, the impedance plot in the complex plane (solid line in Figure 3) assumes the form of two semicircles in the high and low-frequency range. In the case of the lower equivalent circuit shown in Figure 2, the second semicircle ends with the turn and the linear increase of impedance at low frequencies (dashed line in Figure 3).

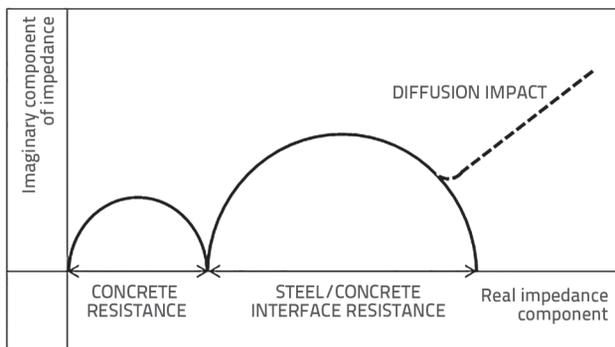


Figure 3. Schematic representation of impedance spectrum in complex plane

Half-diameter of the low-frequency impedance semicircle obtained on the basis of the equivalent circuits model points to the corrosion resistance at the steel/concrete interface [19]. Half-diameter of the high-frequency impedance semicircle indicates the resistance of concrete layer. In Figures 4.a to 4.e, which show the metering results, only semiconductor parts are visible, and model parameters are obtained by adapting the model with metering data. From the impedance spectra shown in Figure 4, the maximum impedance of the steel/concrete interface is exhibited by a sample without additives (C), and the smallest impedance by a sample with NaCl without inhibitor (C + NaCl). Middle impedance values are observed in samples of INH C and INH B, while as to inhibited samples, the lowest impedance value is exhibited by a sample with INH A inhibitor. The impedance of all samples changes over time. Samples with INH B and INH C retain a relatively high impedance values throughout the test. At the last measurement, the sample with the addition of INH B takes the impedance very close to the chloride-free sample. Diffusion influences occur in systems with chlorides only, without inhibitors at all exposure times and with inhibitor INH A and chlorides for longer exposure times of  $\geq 33$  days. The same samples have very low impedance values throughout the test. The described impedance behaviour at the steel/concrete interface is shown in histogram in Figures 5 and 6.

High impedance retention during the test, and an absence of diffusion control of the corrosion reaction, indicate the inhibition of corrosion by the tested concrete additives INH B and INH C. It can be said that the harmful effect of chloride is greatly reduced by the addition of an effective inhibitor.

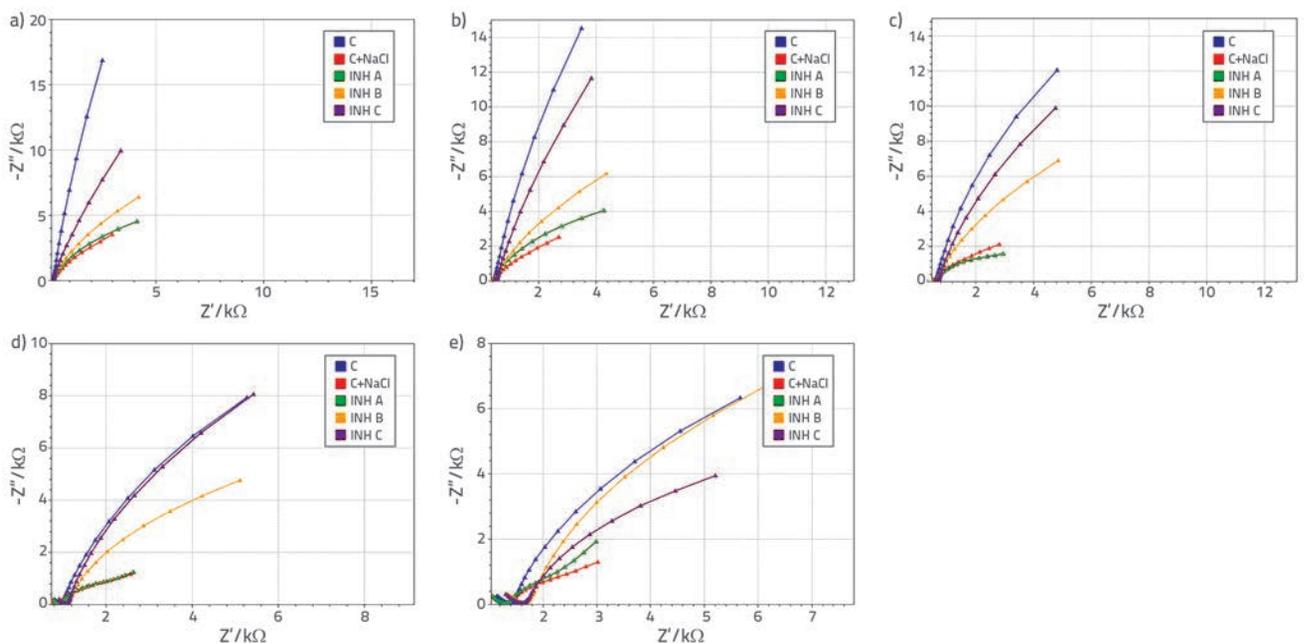


Figure 4. Impedance spectra in Nyquist plot for different systems after a) 6 days, b) 23 days, c) 33 days, d) 54 days and e) 76 days

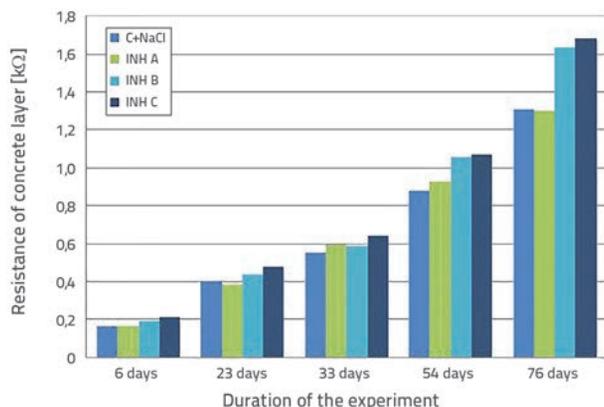


Figure 5. Resistance change of concrete protective layer with time

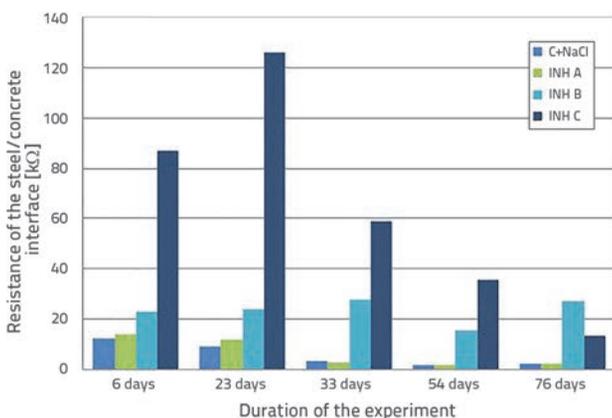


Figure 6. Resistance change on boundary phase with time

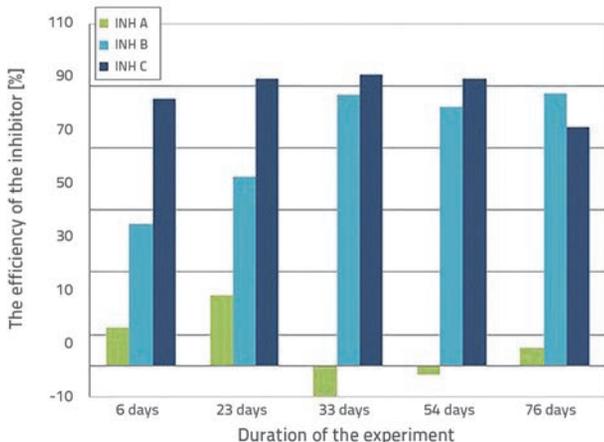


Figure 7. Effectiveness of inhibitors over time



Figure 8. Typical appearance of steel plates after removal of cylinders with concrete and exposure to corrosive environment. Samples shown from left to right are: without chlorides, with chlorides, and with chlorides and inhibitors INH A, INH B and INH C

The histogram shown in Figure 5 reveals a change in the resistance of the concrete protective layer, which increases with time. The values of concrete layer resistance of samples are close, but the last measurement shows a significant increase in resistance for samples with inhibitors INH B and INH C.

By comparing the histogram in Figure 5 showing the resistance of the concrete layer, with the histogram in Figure 6 showing the resistance of the steel/concrete interface, it can be observed that the total resistance is dominated by the resistance of the steel/concrete interface, and it can therefore be assumed that this resistance also reflects the activity of the inhibitor [19-21]. Systems with the addition of INH B and INH C exhibit extremely high resistance of the steel/concrete interface, which is considerably higher than the resistance of the control sample with and without the addition of chlorides.

It should be emphasized that a non-inhibitory and chlorine-free sample, whose resistances are not shown in the figures, has a very high initial steel/concrete interface resistance of 506200  $\Omega$ , which significantly decreased during the experiment to 22690  $\Omega$ . On the other hand, the resistance of the concrete layer without inhibitors and chlorides is comparable to that of other samples, and grows during the experiment from 165 to 1428  $\Omega$ . This behaviour of the impedance components points to the correctness of the equivalent circuit model interpretation. The inhibitor efficiency was calculated according to the following equation::

$$\eta [\%] = \frac{R_0^{-1} - R_{INH}^{-1}}{R_0^{-1}} \times 100 \quad (1)$$

where the steel/concrete interface resistance in the non-inhibitor system is represented by  $R_0$  and in the system with inhibitor by  $R_{INH}$ . The histogram containing the calculated efficacy of the inhibitor system (Figure 7) shows that inhibitors INH B and INH C are very effective in preventing corrosion of the steel substrate, and that their efficacy elapses with time. The effectiveness of INH A, unlike INH B and C, oscillates around zero. Oscillations can be explained by passivation and depassivation of surface portions, which is a characteristic behaviour of steel surface in the partially passivating environment. The efficacy value averaged over the entire study period is 90.9 % for INH C, 70.9 % for INH B, and 5.6 % for INH A. Relatively stable values for highly effective B and C inhibitors are seen to occur after 33 days,

which enables shortening of the experiment implementation time. This time is much shorter than the one normally required according to the ASTM-G109 method.

### 3.2. Sample appearance after measurement

Immediately after completion of the measurement, the steel surface is covered with a white-grey coating that reflects the passivity of the steel, which is the result of contact with concrete with a high pH. Figure 8 shows the appearance of metal surface after completion of measurement and two-week exposure to the corrosive environment with about 50 % RH.

In a partially passivated surface, an active-passive corrosion cell is created, which promotes corrosion of unprotected surface parts. High corrosion on the non-inhibitor sample with the addition of chlorides was observed, while corrosion is little less pronounced on the sample without the addition of inhibitors and chlorides. The sample with INH A shows signs of corrosion, while the remaining two samples remained unaltered. The difference in the uniformity and thickness of the grey-white layer on the metal surface is visually observed. The layer is homogeneous and thicker in samples with inhibitors INH B and INH C, while situation is the worst in non-inhibitory samples. The visual appearance of the samples correlates well with the impedance measurements results.

## 4. Conclusion

This paper investigated the possibility of testing effectiveness of corrosion inhibitors in concrete by adapting the standard method HRN EN ISO 16773 to the required purpose. The specific construction of the measuring cell enabled activation of impedance spectra, from which conclusions can be reached about:

- the mechanism
- the efficiency
- the time dependence of the inhibitor efficiency
- the visual inspection of the metal surface can be completed upon completion of the measurement.

Three organic corrosion inhibitors were tested. Based on the research, it can be concluded that the migrating INH C inhibitor is most effective in corrosion inhibition (average efficiency value is 90.9 %), and its efficacy does not change significantly over time. INH B also has a high steady average efficiency value of 70.9 %, and the last measurement shows almost identical behaviour of the system with chlorides and INH B and pure mortar systems without the addition of sodium chloride. Inhibitor INH A shows an increase in efficacy at the initiation of measurement of up to about 20 %, but later its efficiency decreases, only to increase once again at the end of the measurement (average efficacy value is 5.6 %).

It was found that the presence of chlorides in concrete most reflects on the resistance of the steel/concrete interface, that is, exactly where the corrosion inhibitor is active. The speed of testing and the possibility of quantification of inhibitory efficacy are the main advantages of the tested method prior to the prevalent ASTM-G109 method which, most likely due to its slowness and its qualitative nature, has not found its place in European standardization practice.

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## REFERENCES

- [1] Yoon-Seok, C., Jung-Gu, K., Kwang-Myong, L.: Corrosion behavior of steel bar embedded in fly ash concrete, *Corrosion Science*, 48 (2006), pp. 1733-1745, <https://doi.org/10.1016/j.corsci.2005.05.019>
- [2] Böhni, H.: *Corrosion in reinforced concrete structures*, 1<sup>st</sup> edition, Woodhead Publishing Limited, Cambridge, 2005, <https://doi.org/10.1533/9781845690434>
- [3] HRN EN 206:2016 Beton - Specifikacija, svojstva, proizvodnja i sukladnost (EN 206:2013+A1:2016)
- [4] Youping, L.: *Modeling the Time-to-Corrosion Cracking of the Cover Concrete in Chloride Contaminated Reinforced Concrete Structures*, Faculty of the Virginia Polytechnic Institute and State University Blacksburg, Virginia, dissertation, pp. 1, 7, 12, 1996.
- [5] Ukrainczyk, N.: *Predviđanje korozije armature u betonu pri maritimnim uvjetima pomoću živčevne mreže*, Fakultet kemijskog inženjerstva i tehnologije, diplomski rad, Zagreb, 2004.
- [6] Hansson, C.M., Mammoliti, L., Hope, B.B.: Corrosion inhibitors in concrete - Part I: The principles, *Cement and Concrete Research*, 28 (1998) 12, pp. 1775-1781, [https://doi.org/10.1016/S0008-8846\(98\)00142-2](https://doi.org/10.1016/S0008-8846(98)00142-2)
- [7] HRN EN 1504-9 Proizvodi i sustavi za zaštitu i popravak betonskih konstrukcija - Definicije, zahtjevi, kontrola kvalitete i vrednovanje sukladnosti - 9. dio: Opća načela za uporabu proizvoda i sustava (EN 1504-9:2008)
- [8] Cortec Corporation, <https://www.cortecvci.com/Publications/Brochures/MCIBrochure/MCI.pdf> pristup 19.09.2017.
- [9] Miksic, B.A.: *Improving Durability of Infrastructure with Migratory Corrosion Inhibitors (MCI®)*, FNACE, handbook, 2014.
- [10] ASTM G109 - 07(2013) Standard Test Method for Determining Effects of Chemical Admixtures on Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments

- [11] HRN EN ISO 16773:2016 Elektrokemijska impedancijska spektroskopija (EIS) na visokootpornim prevučenim uzorcima - 1. dio: Nazivi i definicije (ISO 16773-1:2016; EN ISO 16773-1:2016)
- [12] HRN EN ISO 16773:2016 Elektrokemijska impedancijska spektroskopija (EIS) na visokootpornim prevučenim uzorcima - 2. dio: Prikupljanje podataka (ISO 16773-2:2016; EN ISO 16773-2:2016)
- [13] HRN EN ISO 16773:2016 Elektrokemijska impedancijska spektroskopija (EIS) na visokootpornim prevučenim uzorcima - 3. dio: Obradivanje i analiza podataka iz slijepih ćelija (ISO 16773-3:2016; EN ISO 16773-3:2016)
- [14] HRN EN ISO 16773:2017 Elektrokemijska impedancijska spektroskopija (EIS) na visokootpornim prevučenim uzorcima - 4. dio: Primjeri spektra polimerom prevučenih uzoraka (ISO 16773-4:2017; EN ISO 16773-4:2017)
- [15] Montemor, M.F., Simões, A.M.P., Salta, M.M., Effect of fly ash on concrete reinforcement corrosion studied by EIS, *Cement & Concrete Composites*, 22 (2000), pp. 175 - 185, [https://doi.org/10.1016/S0958-9465\(00\)00003-2](https://doi.org/10.1016/S0958-9465(00)00003-2)
- [16] HRN EN 196-3:2016 Metode ispitivanja cementa - 3. dio: Određivanje vremena vezivanja i postojanosti volumena (EN 196-3:2016)
- [17] Trépanier, S.M., Hope, B.B., Hansson, C.M.: Corrosion inhibitors in concrete Part III. Effect on time to chloride-induced corrosion initiation and subsequent corrosion rates of steel in mortar, *Cement and Concrete Research*, 31 (2001), pp. 713-718, [https://doi.org/10.1016/S0008-8846\(01\)00470-7](https://doi.org/10.1016/S0008-8846(01)00470-7)
- [18] Monticelli, C., Frignani, A., Trabanelli, G.: A study on corrosion inhibitors for concrete application, *Cement and Concrete Research*, 30 (2000), pp. 635-642, [https://doi.org/10.1016/S0008-8846\(00\)00221-0](https://doi.org/10.1016/S0008-8846(00)00221-0)
- [19] Trabanelli, G., Monticelli, C., Grassi, V., Frignani, A.: Electrochemical study on inhibitors of rebar corrosion in carbonated concrete, *Cement and Concrete Research*, 35 (2005), pp. 1804- 1813, <https://doi.org/10.1016/j.cemconres.2004.12.010>
- [20] Chaparro, W.A., Ruiz, J.H.B., Gómez, R.J.T.: Corrosion of reinforcing bars embedded in alkali-activated slag concrete subjected to chloride attack, *Materials Research*, 15 (2011) 1, <https://doi.org/10.1590/S1516-14392011005000096>
- [21] da Silva, F.G., Liborio, J.B.L.: A study of steel bar reinforcement corrosion in concretes with SF and SRH using electrochemical impedance spectroscopy, *Materials Research*, 9 (2006) 2, <https://doi.org/10.1590/S1516-14392006000200018>