CATIONIC CORROSION INHIBITORS AND THEIR MIGRATION ABILITY IN REAL CONCRETE SPECIMENS

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Abstract

Corrosion of reinforcing steel is one of the main reasons of reinforced concrete structures deterioration, which is caused primarily by chlorides. Electrochemical chloride extraction (ECE) and electrochemical injection of corrosion inhibitor (EICI) are promising techniques eliminating this adverse effect. Both the techniques are based on application of electric field. Electrochemical chloride extraction from a reinforced concrete structure may be accompanied with an electrochemical injection of healing agents if such agents are positively charged and are able to migrate towards the activated reinforcement. The right choice can be positive charge carried by cationic corrosion inhibitors. Tests have been applied on real samples of concrete with various corrosion inhibitors using diffusion or migration methods. After the corrosion inhibitor application, the migration ability of the individual inhibitors was monitored. Comparison of migration ability of inhibitors was based on concentration profile in various depths. In addition to migration, corrosion inhibitors have been tested for sufficient corrosion inhibition efficiency that was studied in chloride containing concrete pore solution.

Keywords: Concrete, reinforcement corrosion, electrochemical chloride extraction, injection of corrosion inhibitors

1. INTRODUCTION

A reinforced concrete is economical and widely used construction material. However, reinforcing steel in the concrete is often subject to corrosion damage [1]. The steel embedded in fresh concrete is covered on its surface by a thin layer of iron oxide, because of a high alkalinity of pore water in the concrete. The pH ranges are from 12.5 to 13 in the concrete, therefore steel stays in a passive state in agreement with the Pourbaix diagram of iron [2,3]. A process of corrosion in the concrete is most often done in two ways. The first one is accelerating steel corrosion by carbonation of concrete. Formation of $CaCO_3$ by reaction of carbon dioxide from the atmosphere reduces the alkalinity of the concrete [4]. The formed thin rust layer on the steel has no protection character, that's why the steel is very sensitive to corrosion in the medium of pH-region of the iron-water system [2]. Second mechanism is penetration of chloride ions (originate from seawater and de-icing salt, etc.) into the concrete pore system to cause an extensive pitting corrosion of steel reinforcement [5]. Level of the chloride ion in the concrete may be reduced by the use various methods, which can achieve recovery of passive layer.

One of the possible examples is cathodic protection or cathodic prevention. However, cathodic prevention is designed to protect steel in concrete even before the onset of chloride-induced corrosion [6,7]. Other possible way to recovery reinforcement concrete structure je realkalization [8]. To the next method can be an electrochemical chloride extraction. Otherwise also called electrochemical chloride removal. Electrochemical extraction of chlorides uses an electric field with a current density in the range of 1-5 A/m². Such an electric field is introduced into the steel components of the reinforced concrete structure to undergo rehabilitation, with the migration of chloride ions from the concrete for several weeks [9,10]. The second method with using electric field is electrochemical injection of corrosion inhibitors into to concrete. This method is very similar to the

method of electrochemical chloride extraction. While the electrochemical chloride extraction only uses alkaline solution for rehabilitation [11], in this method, corrosion inhibitors are added to the solution. The electric field is introduced between the cathode (in our case it is a steel placed in concrete) and anode. The anode is in most cases external and is located on the surface of the reinforcement concrete structure. It is mesh made of activated titanium or stainless steel immersed in the aqueous solution of a corrosion inhibitor [12].

Corrosion inhibitors can increase the lifetime of a reinforced concrete structure by prolonging the corrosion initiation time (with an increase of the critical chloride threshold) [13]. The reports [3,14] present basic information related to the basic mechanism of study, which gives information about the classification of inhibitors and it's the mechanism of protection.

A corrosion inhibitor suitable for electrochemical injection should fulfill several conditions. Very important is their existence in a cationic form in an aqueous medium under the given conditions. The inhibitor must provide sufficient protection against corrosion in the chloride ion environment. Therefore, corrosion inhibitors based on amine or alkanolamine are a promising choice when stable in their cationic form under given conditions with respect to concrete pore solution pH. These inhibitors may be surface-applied and used to rehabilitate existing structures [15] or pass into hardened concrete through an external electrical mesh.

The aim of this study was to determine the migrating ability of selected corrosion inhibitors to real samples of concrete.

2. EXPERIMENTAL PART

2.1. Corrosion inhibitors

During the experiment, two cationic corrosion inhibitors were tested. All information about them are summarized in **Table 1**. During the experiment concentration of 0.423 mol.l^{-1} for solution was used. This concentration was determined from the critical chloride content for activation of corrosion process. The value of critical chloride content is 0.4 weight % of Cl$^-$ per cement, while at normal humidity concentration of Cl$^-$ will be 15 g.l^{-1} in concrete pore solution. After, this value was converted to mol.l^{-1} and is equal to 0.423 mol.l^{-1} of Cl$^-$.

Table 1 Used corrosion inhibitors

Name	Chemical purity (%)	Molar Weight (g·mol^{-1})	pH of solution	Supplier
Tetrabutylammonium bromide (ReagentPlus®)	≥ 99.0	322.37	6.9	Sigma - Aldrich
Tetrabutylphosphonium bromide	98.0	339.33	4.9	

2.2. Concrete specimens

Real concrete specimens were used for this experiment. For the preparation of 1m^3 of OPC concrete specimens were used the components listed in **Table 2**. From this mixture, concrete cylinder specimens with dimensions of 100 mm in diameter and 50 mm in height were cast. The specimens were kept in water for 28 days. Afterwards, the specimens were dried at 105 °C. As shown in **Figure 2**, unexposed surface of the specimens was painted by a synthetic paint IZOBAN (Detecha). Water-to-cement ratio corresponded to 0.8. This value corresponded to low quality of concrete [16]. Poor quality of concrete been chosen on purpose for accelerating the transport processes.

Table 2 Composition of OPC concrete 1m^3

Components	Mass (kg)
Cement (grade CEM I 42.5R)	262
Water	210
Sand (grain size 4 - 8 mm)	1150
Aggregate (grain size 4 - 8 mm)	291
Aggregate (grain size 8 - 16 mm)	582

2.3. Electrochemical technic

The concrete cylinder was fixed in between two chambers with the volume of 0.5 l for anolyte and catholyte. Stainless steel mesh was built in the chamber parallel to the both flat surface of the concrete specimen at the distance app. 3 mm, how to show in **Figure 1**.
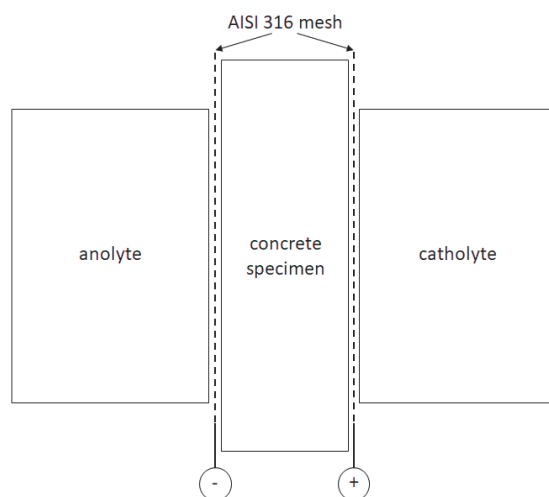
Figure 1 Experimental cell for electrochemical treatment
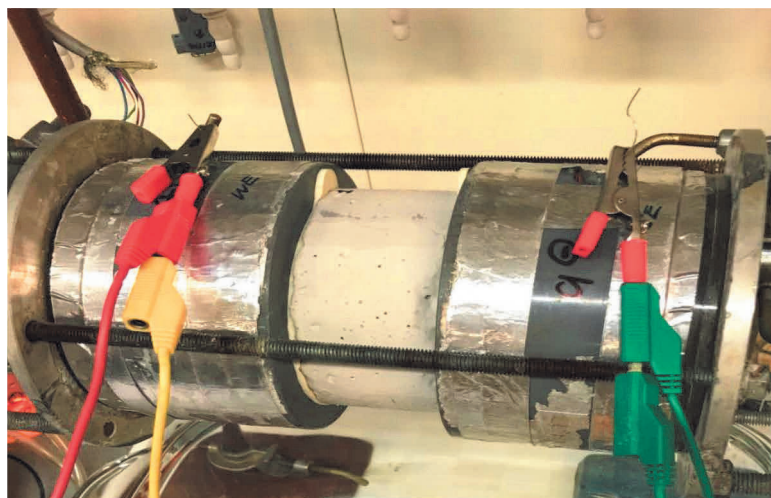
Figure 2 Concrete specimen between anolyte chamber and catholyte chamber

The catholyte chamber (in **Figure 2**, on right side) was filled with 3 % NaCl solution and the anolyte chamber was filled with corrosion inhibitors. Concentration of corrosion inhibitor was 0.423 mol·l^{-1}. Constant current with

value 2.53 mA and 16.65 mA was applied between stainless steel mesh electrodes. These values correspond to current density of 1 A·m^{-2} or 5 A·m^{-2}. Constant current was introduced by the Radelkis OH-404/A potentiostat, which was used as galvanostat. Galvanostatic mode was used for electrochemical chloride extraction with simultaneous electrochemical injection of corrosion inhibitor. The current flow was measured by means of the METEX M 3650 multimeter and recorded by means of the METEX Control Software Client every 5 min. The resulting voltage was recorded by using of the IEC1010-1 voltmeter.

2.4.   Method of analysis

After the extraction and/or injection, two 5 millimeters thick slices were taken from the catholyte (NaCl solution) side of the concrete cylinder and three 5 millimeters thick slices were taken from the anolyte (inhibitor solution) side in order to determine the concentration profile of the injected inhibitor across the concrete cylinder. The slices were pulverized using a laboratory mill and the powder was dried at 80 °C overnight. The amount of 20 grams of the powder was then mixed with 50 ml of distilled water and the mixture was ultrasonicated for 1 hour. The liquid phase was separated from the solid by means of centrifugation and analyzed. The guanidine concentration was determined by a mass spectrometer LC-MS LTQ-Orbitrap Velos. The chloride concentration was determined by an absorption spectrophotometer FIA lab 2000.

The concentration profile obtained by electrochemical injection was compared with that resulting from a plain diffusion. The diffusion experiment was set exactly in the same way as the electrochemical injection, except the current that wasn´t introduced.

3.   RESULTS AND DISCUSSION

3.1.   Tetrabutylammonium bromide (TBAB)

The chloride extraction process (can be seen in **Figure 3 a)**) has been significantly affected by the use of an electric field. While in the test of spontaneous diffusion, the concentration values were small, in units mmol·l^{-1} (concentration of chloride ions or inhibitor in the extract). When current density 1 and 5 A·m^{-2} was applied, the values of concentration of chloride ions increase to tens mmol·l^{-1}. At the highest current density used, chloride ions were able to get through the whole sample at a relatively high concentration, up to app. 7 mmol·l^{-1}. With regard to TBAB, it was injected only within 10-15 mm of the sample surface.

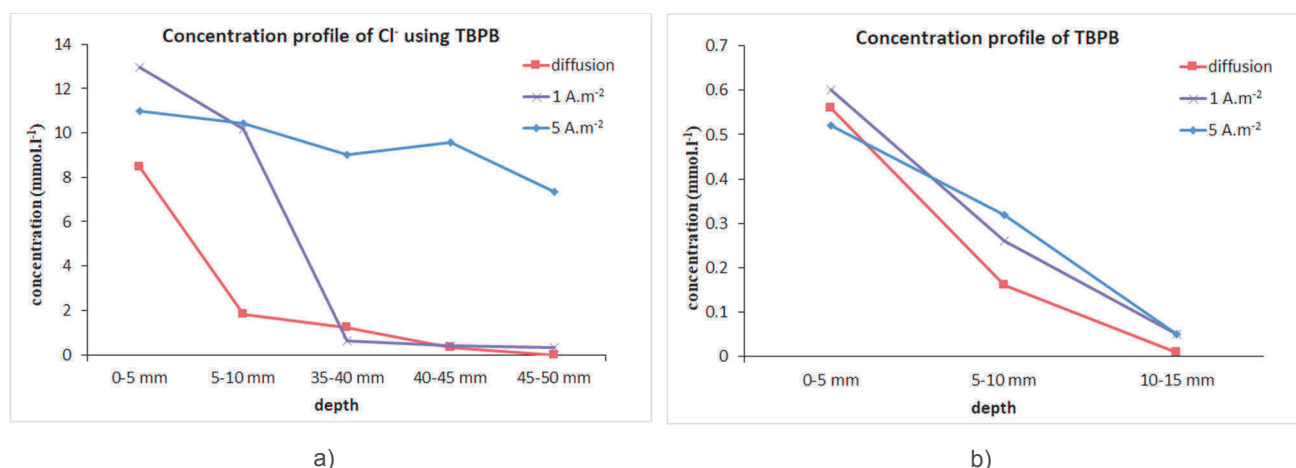a)   b)
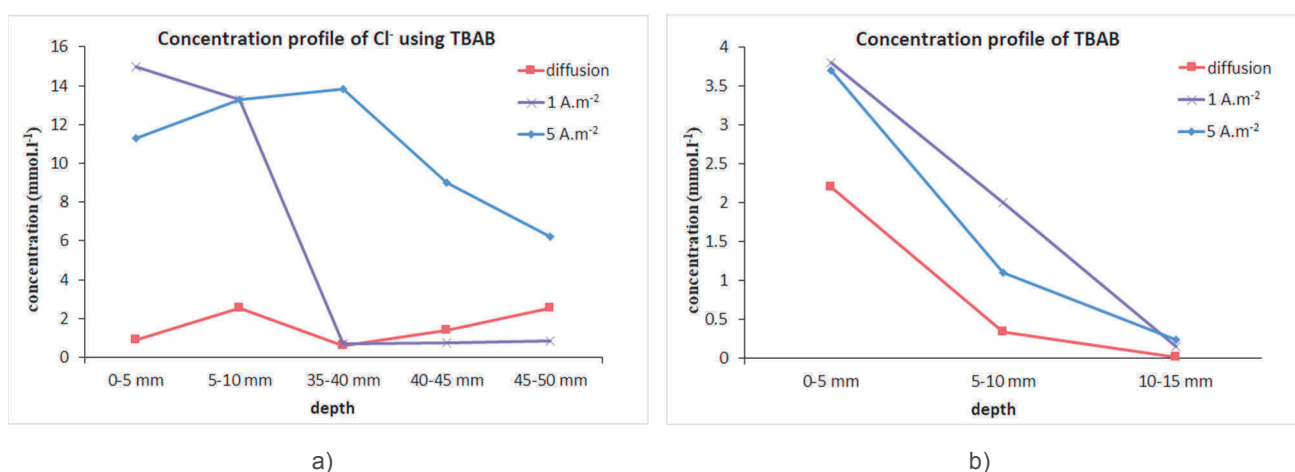
Figure 3 Concentration profiles: a) concentration profile of chloride ions after 7 days exposure and b) concentration profile of TBAB after 7 days exposure

Figure 3 b) shows the concentration profiles for the individual test methods, as without the electric field in the same way and with the established electrical field. As can be seen, during spontaneous diffusion, the inhibitor concentration on the surface of the sample is quite high, but the direction away from the surface concentration rapidly decreases, and the next section/segment is almost undetectable. When using a current density of 1 and 5 A·m^{-2}, the inhibitor concentration on the surface of the sample is almost twice as high. In the second and third sections, the concentration gradually decreases to about 0.2 mmol·l^{-1}. It can be seen from the concentration profile (**Figure 3 b)**) that when applying TBAB, the current density value of 1A·m^{-2} is more advantageous.

3.2. Tetrabutylphosphonium bromide (TBPB)

Figure 4 shows individual concentration profiles as for chloride ions and for inhibitors. During spontaneous diffusion, we observe the same action as that of TBAB, but at 45-50 mm, chloride ions chloride ions haven´t been detected. At the introduction of a current density of 1 A.m^{-2}, the concentration of chloride ion on the sample surface increased, but only to the second cut. The current density of 5 A.m^{-2} appears to be very promising for the extraction of chloride ions. By using this current density, it was possible to get the largest amount of chloride ions through the sample. With respect to the inhibitor, no significant changes have been observed here either in spontaneous diffusion or in the application of the electric field. The values of concentration of corrosion inhibitor were approximately the same for all three methods tested.

a)   b)

Figure 4 Concentration profiles: a) concentration profile of chloride ions after 7 days exposure and b) concentration profile of TBPB after 7 days exposure

4. CONCLUSION

Use electrochemical chloride extraction using a current density of 5 A·m^{-2} appears to be a possible method for removing chloride ions from reinforcement structure. Promising results were obtained when a TBAB was used as a corrosion inhibitor, which at the application of the current density 1 and 5 A·m^{-2} reached a depth of 10-15 mm but the concentration at that depth wasn´t significant.

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REFERENCES

[1]   BROOMFIELD, J. P. *Corrosion of Steel in Concrete, Understanding, investigation and repair*. 2nd ed. Oxon: Taylor & francis, England, 2007. p. 7-9.

[2]   RAUPACH, M., ELSENER, B., POLDER, R. and MIETZ, J. *Corrosion of reinforcement in concrete. Mechanisms, moniotoring, inhibitors and rehabilitation techniques*. 1st ed. Cambridge: Woodhead Publishin Limited, England, 2007. p. 1-2.

[3]   PANDIARAJAN, M. et al. Corrosion inhibitors for concrete corrosion - an overview. *Eur. Chem. Bull.* 2013. no. 1, vol. 2, pp. 1-8.

[4]   KOURIL, M., LOVASI, T.; MSALLAMOVA, S.; NEMECEK, J.; SULC, R. Electrochemical injection of cathionic corrosion inhibitors. In *ACSEE 2017. Sixth International Conference on Advances in Civil, Structural and Environmental Engineering*. Rome, 2017, pp. 40-44.

[5]   LOVASI, T., MSALLAMOVA, S., KOURIL, M., JAMBOROVA, T., STOULIL, J., NEMECEK, J. and SULC, R. Cathionic corrosion inhibitors for protection of steel in chloride contaminated concrete. In *METAL 2017: 26rd International Conference on Metallurgy and Materials.* Brno, 2017, pp. 1361-1367.

[6]   PEDEFERRI, P. Cathodic protection and cathodic prevention. *Construction and Building Materials*. 1996. vol. 10, no. 5, pp. 391-402.

[7]   CARMONA, J., GARCÉS, P. and CLIMENT. M.A. Efficiency of a conductive cement-based anodic system for the application of cathodic protection, cathodic prevention and electrochemical chloride extraction to control corrosion in reinforced concrete structures. *Corrosion Scince*. 2015. vol 96, pp. 102-111.

[8]   MIRANDA, J.M. et al. Several questions about electrochemical rehabilitation methods for reinforced concrete structures. *Corrosion Science*. 2006. vol. 48, pp. 2172-2188.

[9]   SAWADA, S., PAGE, C. L. and PAGE, M.M. Electrochemical injection of organic corrosion inhibitors into concrete. *Corrosion Science*. 2005. vol. 47, pp. 2063-2078.

[10] ORELLAN, J.C., ESCADEILLAS, G. and ARLIGUIE, G. Electrochemical chloride extraction: efficiency and side effects. *Cement and Concrete Research*. 2004. vol. 34, pp. 227-234.

[11] ŽIVICA, Vladimír. Referencing: Elektrochemické postupy pre sanáciu korodovaných železobetónových konštrukcií. *iMateriály* [online]. 2008. [viewed 2018-03-22]. Available from https://imaterialy.dumabyt.cz/rubriky/poruchy/elektrochemicke-postupy-pre-sanaciu-korodovanych-zelezobetonovych-konstrukcii_101507.html.

[12] PAN, T., NGUYEN, T.A. and SHI, X. Assessment of Electrical Injection of Corrosion Inhibitor for Corrosion Protection of Reinforced Concrete. *TRB Annual Meeting 2008*. Washington D.C.

[13] ORMELLESE, M., BOLZONI, F., GOIDANIC, S., PEDEFERRI, MP. and BRENNA, A. Corrosion inhibitors in reinforced concrete structures. Part 3 - migration of inhibitors into concrete. *Corrosion Engineering, Science and Technology*. 2011. vol. 46, no. 4, pp. 334-339.

[14] ABDULRAHMAN, A.S. et al. Corrosion inhibitors for steel reinforcement in concrete: A review. *Scientific Research and Essays*. 2011. vol. 6, no. 20, pp. 4152-4162.

[15] GAIDIS, J. M. Chemistry of corrosion inhibitors. *Cement & Concrete Composites*. 2004. vol. 26, pp. 181-189.

[16] GIRARD, Jeff. Referencing: The importance of water/cement ratio in concrete countertop mix design. The Concrete Countertop Institute [online]. 2011. [viewed 2018-03-25]. Available from http://www.concretecountertopinstitute.com/blog/2011/07/the-importance-of-watercement-ratio-in-concrete-countertop-mix-design