

CATHIONIC CORROSION INHIBITORS FOR PROTECTION OF STEEL IN CHLORIDE CONTAMINATED CONCRETE

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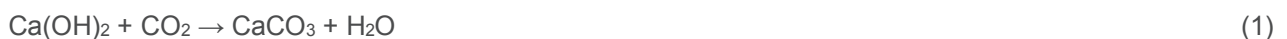
Abstract

Electrochemical chloride extraction from a reinforced concrete structure may be accompanied by an electrochemical injection of healing agents if such agents are positively charged and are able to migrate towards the activated reinforcement. Nanoparticles carrying a positive or cathionic corrosion inhibitors might be the proper choice. Organic substances with a positive charge and their salts are mostly such inhibitors. The essential conditions for successful application of such corrosion inhibitors are their sufficient corrosion inhibition efficiency that was studied and evaluated elsewhere and their stability of positive charge in alkaline concrete environment and their migration ability through concrete pore system.

Keywords: Concrete, corrosion inhibitors, chloride

1. INTRODUCTION

Steel embedded in fresh concrete is largely in a passive state due to the formation of a thin layer of iron oxide on its surface. This passive layer is stable due to the high alkalinity of the concrete, the pH of which ranges from 12.5 to 13 [1]. For corrosive action to take place, this passive layer must be broken. This process is most often done in concrete in two ways. The first way is the penetration of chloride ions through the concrete cover layer up to the steel reinforcement. The chlorides may originate from seawater and de-icing salt but also in admixtures used in concrete production itself. [2]. One of the main research is concerned with the possibilities of reducing the adverse effects of chlorides and of deactivating its catalytic effects [3]. It is assumed that the cement itself has the ability to bind chloride ions to form a Friedel salt which is ineffective as a corrosion catalyst [4, 5]. Consequently, the content of chlorides in concrete is limited, as a result of which terms such as chloride thresholds or critical chloride content [6]. There are many different publications that report on the critical content of chlorides. According to the author [7] this value ranges from 0.6 to 1 kg / m³. However, the European standard EN 206-1 specifies chloride content in the range of 0.2 - 0.4 % of chlorides by mass of binder for reinforced concrete and 0.1 to 0.2 % for pre-stressed concrete [6]. Theoretically, if the critical chloride content is not exceeded, the alkalinity of the concrete is sufficient to minimize corrosion [7]. The second possible way of accelerating steel corrosion in concrete is that the concrete is carbonated. Carbonation occurs as a result of the carbon dioxide reaction from the atmosphere with the concrete, which results in a reduction of the alkalinity of the concrete according to the following reaction [8]:



Carbonation of the concrete causes problems in practice (lowering the pH and lowering the basic protection provided by concrete) only when the concrete layer over the reinforcing steel is not sufficiently thick and the concrete is porous [7, 9]. Once the corrosion starts, it can lead to complete damage of the structure. The corrosion process, like an electrochemical process, takes place on the surface of the steel where the anodic and cathodic regions are located in parallel. The reactions occurring on the steel surface can be summarized as follows [10, 11]:





The rate of corrosion is therefore controlled by the rate of diffusion of oxygen towards the steel reinforcement through the cover layer of concrete [10]. Chloride-induced corrosion can be mitigated by reducing the chloride ion level in concrete by various mechanisms. One of the possible examples is cathodic protection [12]. Other options are thermal acceleration diffusion, removal of chlorides under pressure [13], re-alkalisation and electrochemical extraction [8, 14]. Cathodic protection is aimed at reducing corrosion rate in construction where the chloride process is already under way, it is now necessary to use higher current densities of up to 15 mA / m² or 20 mA / m² [16, 17]. 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 specific components of the structure to undergo rehabilitation, with the migration of chloride ions from the concrete for several weeks [5, 15]. In the connection, the steel reinforcement is a cathode and titanium or stainless-steel mesh is generally used as anode placed in a suitable electrolyte on the surface of the concrete. After connecting the apparatus to a DC power source, the steel will reach more negative potential. This will repel anions and attract cations contained in the concrete pore solution. Sodium, potassium and calcium ions accumulate at the cathode. However, it has been found out that such accumulation intensifies the risk of alkaline-silica reaction in concrete containing potentially reactive aggregates [18]. The foregoing method may be supplemented by the electrochemical injection of the corrosion inhibitor (EICI) shown in **Figure 1**. The arrangement EICI is similar to the electrochemical extraction of chlorides, so that the electric field flows between the steel as the cathode and the outer anode, the whole arrangement being inserted into the electrolyte which adheres to the structure surface [8, 18]. The effects of chloride-induced corrosion can also be mitigated by the use of some chemicals that serve as corrosion inhibitors. Under the action of the electric field, the cationic component of the corrosion inhibitor migrates through the concrete layer to the cathode while the chloride ions in the concrete migrate from the concrete to the anode [19]. The corrosion inhibitor contained in the electrolyte creates a protective layer around the embedded steel rods and isolates corrosive substances such as chlorides and oxygen when the inhibitor concentration reaches the adequate value [20]. At the same time, the alkalinity of the pore solution is increased in the vicinity of the steel reinforcement. This phenomenon has the effect of promoting repassivation of steel. It has been shown that electrochemical injection is an effective way of adding corrosion inhibitors to already existing structures and can be used as a rehabilitation measure to slow down or reduce corrosion. The study showed that injection could provide adequate protection against the corrosion of steel reinforcements in chloride contaminated concrete [21]. This technology is new and has a non-destructive nature requiring only a temporary installation (10-15 days). According to the National Association of Corrosion Engineers (NACE), the current density used should not exceed 4 A / m² of steel surface and the charge used during the treatment should not exceed 1500 Ah / m² [21]. While electrochemical chloride extraction and electrochemical injection of corrosion inhibitor technologies look like promising techniques for the treatment of ferro-concrete structures contaminated with chlorides, their application is currently limited by detailed information about basic mechanisms [22].

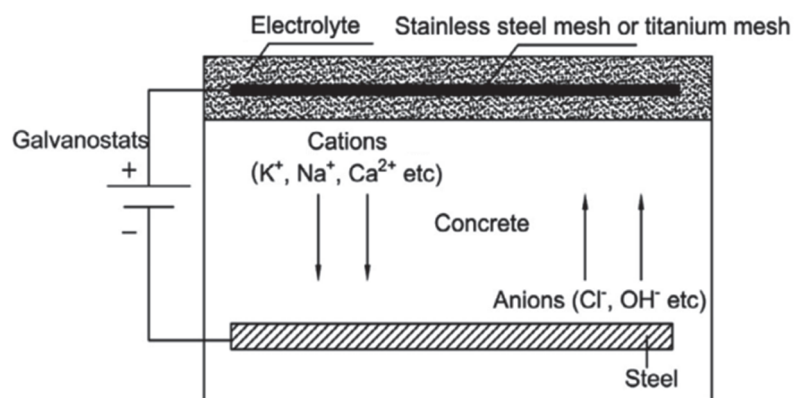


Figure 1 Schematic connection of EICI [20]

Such inhibitors may be surface-applied and used to rehabilitate existing structures [20] or pass into hardened concrete through an external electrical mesh. However, the mitigating mechanism involves a complex electrochemical process that depends primarily on the concentration of

chloride ions relative to the concentrations of corrosion inhibitors [6]. The efficiency of a corrosion inhibitor in mitigating chloride-induced corrosion can be simplistically determined by laboratory tests in a simulated pore solution concurrently containing the inhibitor and chloride ions at a given concentration while simultaneously investigating the corrosion rate over time. Prediction of inhibitor and chloride ion concentrations on the steel surface in concrete after application of the electric field requires extensive modelling research. The movement of chloride ions and corrosion inhibitor ions can be attributed to three fundamental mechanisms, namely natural diffusion, electrical migration, and transport by the movement of the pore solution due to capillary forces or an external pressure gradient [14]. In water-saturated concrete, chloride ions migrate preferably by natural diffusion and electrical migration, if an electrical field is applied [22]. The natural diffusion of chloride ions depends primarily on their concentration gradient, which can also be influenced by the electrical membrane potential generated in the concrete [22]. An external electric field is often used to control the transport of chloride ions and protective species in concrete [22]. Corrosion inhibitors can become a good choice for other protection methods or traditional repair methods that are already in use due to lower costs and possible simple use. Classification of corrosion inhibitors is varied, as there are several options for distributing corrosion inhibitors. Mainly used classifications include division according to application methods or protective mechanism.

According to the application methods, the corrosion inhibitors can be divided according to the concrete into which it is added whether the inhibitor is added to fresh concrete or is already applied to the hardened concrete. According to the protection mechanisms, corrosion inhibitors can be divided into anodic, cathodic and mixed corrosion inhibitors. Anodic corrosion inhibitors act to dissolve steel and to reduce corrosion rates by increasing the corrosion potential of steel while cathodic inhibitors act on the oxygen reaction on the steel surface and reduce corrosion rate by reducing corrosion potential. The function of cathodic inhibitors is that they act on the oxygen reaction on the steel surface and they reduce the corrosion rate. The last group is mixed corrosion inhibitors, which simultaneously act on both anode and cathode sites and reduce corrosion rate without significant change in corrosion potential. This type of inhibitor has a hydrophobic group and a polar group such as -N, -S, -OH [22, 24]. Great attention is dedicated to the corrosion inhibitor with a positive charge and the possibility of application to hardened concrete [25, 26]. As far as chlorides are concerned, mostly sodium, calcium or magnesium diffuse into the concrete environment, which does not significantly alter the corrosion process [7]. Some of these corrosion inhibitors are based on amines, alcohols or compounds known to have a tendency to diffuse at a noticeable distance through concrete under certain conditions. [23, 24] When introducing these corrosion inhibitors through the surface into an already existing concrete structure, it is assumed that they can reach a sufficient concentration up to the level of the built-in steel reinforcement to protect it from corrosion. The selection of suitable corrosion inhibitors is the key to the success of electrochemical injection. A corrosion inhibitor suitable for electrochemical injection should fulfill several conditions. E.g. to provide sufficient protection against corrosion in the chloride ion environment or to exist predominantly as a cationic species. Therefore, corrosion inhibitors based on amine or alkanolamine are a good choice when considering these conditions [20]. Several researchers have recently studied diffusion rate or absorption-induced penetration of surface-applied inhibitors into concrete and their effectiveness in controlling corrosion of steel under various conditions [23].

As mentioned above, a properly chosen inhibitor may affect the on-going process on the reinforcing steel surface. There are many inhibitors tested in literature, which individual authors undergo in a variety of tests. Highly investigated inhibitors are organic amines and alkanolamines (AMA) inhibitors and their salts with organic and inorganic acids or aminoalcohols [24]. Chelating agents include organic corrosion inhibitors which can form five or six membered chelate rings [24]. These rings are formed by a bond between two or more functional groups from an inhibitor (such as -NH₂, -OH, -SH, -COOH and -SO₃H) and a metal cation [24]. Some studies state that AMA and associated radicals form a layer on the surface of steel that completely covers all anodic and cathodic components and therefore are mixed type inhibitors. In other publications [24], further studies (with potentiodynamic polarization) indicate that amine-based inhibitors and alkanolamines act mainly

on anodic activity, with the consequent increase in corrosion potential. As mentioned in [7], where the author of an example of two inhibitors, namely aminoalcohols such as ethanolamine (C_2H_7NO) and dimethylethanolamine ($C_4H_{11}NO$), which control corrosion by attacking cathodic activity, blocking sites where oxygen picks up electrons and is reduced to hydroxyl ion. Another inhibitor already added to said inhibitor is guanidine carbonate ($C_2H_{10}N_6 \cdot CH_2O_3$). Guanidine carbonate was tested together with ethanolamine in [23]. Both of these inhibitors were introduced into saturated samples of carbonated and non-carbonated concrete with the help of an external electrolyte under the influence of an electric field which was introduced between the steel cathode and the external anode as shown in **Figure 2**. The current density applied to the samples was controlled with a galvanostat and ranged from 1 - 5 A / m² for 3-14 days. Experiments with the same samples and inhibitors were carried out, but without the use of a current. After the injection, the sample

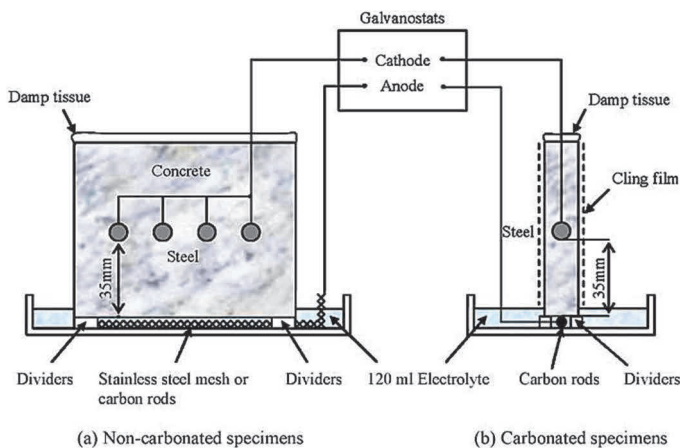


Figure 2 Experimental arrangement [23]

underwent an analysis to determine the concentration profile of the corrosion inhibitor in the concrete using an ion chromatograph.

The efficiency of injection of both inhibitors under the applied electric field was found to be much higher in carbonated concrete than in non-carbonated concrete. Also observed in the samples of scorched concrete, the inhibitors were concentrated near the embedded steel. In non-carbonated concrete, the penetration of guanidine was accelerated to a certain extent by the applied electric field. However, the penetration by ethanolamine was not significantly increased by application of the electric field.

These findings were explained in terms of the

influence of pH values of pore solutions in different samples. Another influence has been attributed to the various degrees of ionization of the respective organic bases, and thus their tendency to migrate and neutralize the cathodically formed hydroxyl ions. A further series of investigations of ethanolamine and guanidine have been elucidated in [19]. Subsequently, the results were used to develop the mathematical model [25].

Karthick et al. [14] increased the number of inhibitors tested and, in addition to guanidine, also tested thiosemicarbazide (CH_5N_3S), ethyl acetate ($CH_3COOC_2H_5$) and triethanolamine ($C_6H_{15}NO_3$) in contaminated concrete with chlorides. For EICI, the current density was 0.5 A / m². At the same time with the electrochemical injection, the amount of chloride ions removed from the cover layer of concrete was monitored. Several methods were used to evaluate injection efficiency, including open circuit potential monitoring followed by potentiodynamic polarization studies before and after EICI. And the last method was impedance measurement before and after EICI. Other methods were the gravimetric method of weight loss, estimation of chloride profiles and surface examination (FTIR, SEM, EDAX and MIP studies). All electrochemical measurements point to the improvement of the steel reinforcement properties after EICI. According to Pan et al. [22] Electric injection of corrosion inhibitor (EICI) shows the potential for protecting the reinforcement against the attack of chlorides using a corrosion inhibitor on the surface of the reinforcement under the influence of an applied external electric field. For the study, eight inhibitors were selected, namely Tetrabutylammonium Chloride (TBA-C), Tetrabutylammonium Bromide (TBA-B), Tetraethylammonium Bromide (TEA-B), Tetramethylammonium Bromide (TMA-B), Tetramethylammonium Chloride (TMA-C), Tetrabutylphosphonium Bromide (TBP-B), Triethanolamine (TEOA) and Tetraethylammonium Chloride (TEA-C). The inhibitory efficacy was tested, expressed as percentage reduction in corrosion rate, was tested using an inhibitor relative to the control sample. The solutions were adjusted to pH 12 with sodium hydroxide, followed by addition of 0.5 M sodium chloride to help simulate the aggressive environment. The control solution was used without the addition of an inhibitor. To the remaining solutions, individual 20 mM inhibitors were added. An open circuit potential (OCP)

measurement was performed. For corrosion rate measurement, a potentiodynamic weak polarization measurement was used. The highest efficacy was achieved in TBA-B (85 %) and also in TMA-C (75 %), the least effective being TEA-C, which reached 18%. Also, Nguyen et al. in [21], were electrically injected using tetrabutylammonium bromide (TBAB) at a current density of 5 A/m² in repair mortar. Testing took place in two electrolytes (0.1 M NaOH and 0.1 M Na₃BO₃) and for two time periods (1 and 4 weeks). The concentration of the organic inhibitor on cation-based was determined before and after EICI using UV-Vis spectroscopy. Experimental results show that EICI treatment with 0.1 M Na₃BO₃ was more effective at inhibitor injection and improved resistance to chloride penetration due to the use of 0.1 M NaOH as an electrolyte. After the 4-week treatment of EICI, the apparent diffusion coefficients of chloride anion in cement mortar were reduced by 40 %. Using EICI, it was possible to halt the corrosion of steel reinforcements caused by chlorides and support passivation of the steel.

2. CONCLUSION

In this paper, several corrosion inhibitors were summarized as a short overview. Using literature, the knowledge of the possible application and parameters appropriate to EICI application was collected. The methods used to monitor the efficacy of individual inhibitors after injection into the concrete structure have also been summarized. However, it was not possible to mention all of the methods tested so far, but their brief overview can be found [1]. Our role in the experimental part is to clarify the functionality and the possibility of using the selected corrosion inhibitors during the rehabilitation of the reinforced concrete structure under the parallel extraction of chlorides and electrochemical injection. In the next timeframe, our selected corrosion inhibitors are tested in simulated solutions of non-carbonated and carbonated concrete. Subsequently, the same inhibitors are subjected to the migration test through a real sample of concrete to determine their ability to pass through the cover layer of concrete using an external electric field. Experiments on concrete samples with steel reinforcement will be the last. Resistometric sensors are added to the reinforcement to determine the change in corrosion rate during injection. This measurement will then be accompanied by measurements of the polarization resistance before and after injection. Another method will be the EIS measurement with which Dr. J. Fojt will help us. When determining concentration profiles and other analytical methods, Dr. S. Msallamová will help us.

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