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Organic substances as corrosion inhibitors for steel in concrete – an overview

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Abstract

Organic inhibitors have attracted considerable attention due to their promising application as admixtures in concrete protecting against corrosion of rebars. Over the last decade the use of those inhibitors significantly raised. The inhibition efficiency depends on their physical and chemical properties. This paper gives short overview of the protection of steel in concrete against the ingress of chlorides, oxygen and carbon dioxide in concrete, as species causing the corrosion of rebars. This work involves only organic inhibitors.

Keywords: Reinforced concrete; organic inhibitors; corrosion; admixtures

1. Introduction

Reinforced concrete is one of the most widely used material in building industry. This is attributed primarily to simplicity of application and low cost of its production. Concrete has high pH in which reinforced steel remains passivated and is highly resistant against corrosion. Corrosion may be defined as the process of material degradation under reactions with its environment or as an internal process, e.g. alkali-aggregate reaction in concrete. Steel in concrete undergoes corrosion through chemical or electrochemical reactions between steel and environment. Rate of the corrosion process depends on the quality of concrete, so high permeability or appearance of cracks accelerates the rate of steel degradation. Corrosion results in the formation of rust, which has different structural and mechanical properties than non-corroded material. The newly-formed rust occupies a higher volume than non-corroded steel and a less homogeneous structure. Rust as a corrosion product expands in volume taking up a volume a few times greater than the original volume, creates internal tension and reduces the strength capacity of steel. Expanding rust thus creates tensile and flexural stress in concrete, leading to the loss of bond between steel and concrete, cracking, delamination and spalling.

In spite of wide use of steel in concrete, in fact this apparently non-corroding material very often undergoes corrosion. This process is caused by salts penetration into bulk concrete, carbonation of concrete or lack of oxygen (Diamanti et al. 2010). Salt, which is used for deicing in winter or sea salt, is an ionic compound which easily dissolves in water and becomes an aggressive agent towards concrete structure. Concrete as a porous

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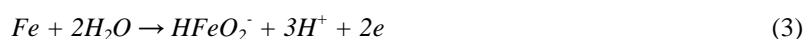
material enables deep penetration of aggressive ionic species. Chlorides from sea salt, de-icing salt, concrete admixtures, unwashed sea sand move easily into concrete and damage the passive layer, applied for steel protection. Ions like chlorides cause local depassivation of the steel leading to pits formation and growth of rust on the rebars (Gaidis 2004). In spite of the relation of between humidity and gas saturation in concrete, where with higher humidity, CO₂ and O₂ transport inside concrete is lower, mentioned gases causes also corrosion. Although the corrosion caused by chloride as pitting process is a localized form of corrosion the corrosion rate increases as well as the area affected by the process.

Steel in concrete is commonly prevented against corrosion by inorganic inhibitors. They have been widely proven in literature as efficient corrosion inhibitors, however some of them like nitrites are toxic or not authorized in some countries (Valek et al. 2007; Jamil et al. 2003). Other inorganic inhibitors are less efficient than nitrites, so organic compounds like amines, alkanolamines, carboxylates, their derivatives and other chemicals are intensively studied as corrosion inhibitors.

2. Basic mechanism of steel corrosion in concrete

In reinforced concrete, the surface of steel is covered by a passive oxide film, which prevents the reinforced bars from corrosion. That passive layer is stable when the pH is greater than 11.5 – 12 (Sheban et al. 2007; Berke and Hicks 2004). Concrete is alkaline with typical value of pH for cement ranging between 12 and 14. However, under the carbonation process it becomes less alkaline and steel corrosion occurs. During carbonation process carbon dioxide penetrates the concrete, where it reacts with hydroxides. That produces carbonates and water decreasing the pH, this in turn breaks down the passivation layer on the steel. Dry portland cement is a mixture of oxides, dominated by CaO and SiO₂. After mixing with water, a calcium oxide hydrates to form portlandite [Ca(OH)₂], which can react with carbon dioxide and forms CaCO₃. The CaCO₃ occupies higher volume than Ca(OH)₂ and seals porous concrete (Kurdowski 2014). Despite the very low rate of this process and lack of its direct influence on the rate of corrosion, it changes the structure of concrete and the permeability for water and ions like chlorides. Although chlorides have only small influence on pH, their presence has effect on depassivation of the protective films inducing pitting corrosion (Saremi and Mahallate 2002).

Depending on the pH near the steel surface and oxygen availability the corrosion of iron rebars can be represented by the following reactions:

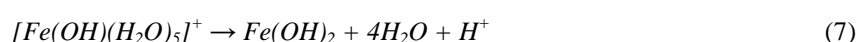
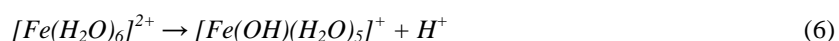


Oxygen has the most detrimental effect on steel rebars. Without oxygen steel rebars in alkaline media do not undergo corrosion even in the presence of aggressive species like chloride ions (Pourbaix 1966; Pourbaix 1974). Resistance against corrosion decreases with higher concrete permeability of chloride ions.

The main anodic reaction which takes place in concrete is (Bastidas et al. 2015):

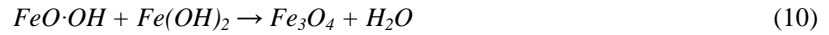
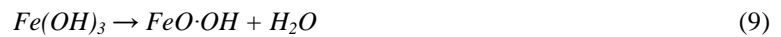
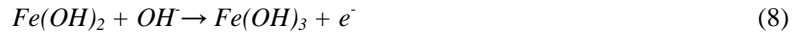


Pits in metal are promoted by the chloride ions and they grow due to the following reactions, where the anodic oxidation produces hexaaquo iron (II), (5) (Sastri 2001):

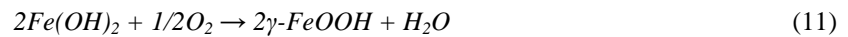


Increased acidity causes propagation of such reactions (5) and (6). Fe(OH)₂ is amphoteric in nature, unstable and quickly form Fe(OH)₃ (8). Fe(OH)₂ forms Fe(OH)₃ under the water and oxygen presence. In alkali

environment $\text{Fe}(\text{OH})_2$ forms $\text{Fe}(\text{OH})_3$, due to the reaction (8). Moreover $\text{Fe}(\text{OH})_2$ with chloride ions may form also FeOCl_2^{2-} and FeCl_2 , which induces the corrosion of steel in concrete (Ryu et al. 2016).



In absence of aggressive species like chlorides or without concrete carbonation both ions Fe^{2+} and Fe^{3+} are stable (Berke 2015), however in presence of chloride ions Fe^{2+} is more stable and over time it forms hydrated ferric oxide $\text{FeO}\cdot\text{OH}$. Instead of the transformation of $\text{Fe}(\text{OH})_2$ into the $\text{Fe}(\text{OH})_3$ the passive oxide $\text{FeO}\cdot\text{OH}$ is formed due to the reaction:



Unfortunately despite higher stability of $\text{FeO}\cdot\text{OH}$ (Lavrynenko 2011) than Fe^{2+} , a drop of pH in concrete below 11 results in initiation of the corrosion process. In Figure 1 the pitting corrosion is presented (Sastri 2001).

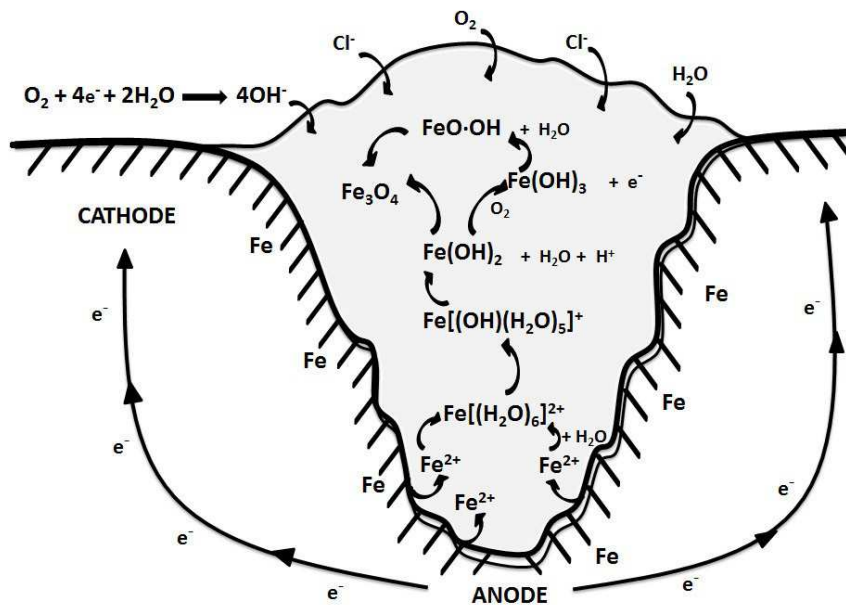


Fig. 1. Graphical representation of corrosion process in pits under chlorides, water and oxygen attack.

Among many causes of the concrete degradation, two major causes of corrosion are the presence of aggressive ions like chloride and gases like carbon dioxide. According to the electrochemical series determining reactivity of metals, iron undergoes corrosion in acidic media and is not resistant to oxidation. Most corrosion processes are combinations of physico-chemical and electrochemical reactions or are strictly electrochemical in nature. Anodic sites on steel with metallic iron occur in spite of the steel covering with protective layer (Söylev et al. 2008).

Iron may undergo corrosion and change from a metallic state into an oxidized state. Corrosion often starts at anodic sites (4) on the metal surface and is an electrochemical process in nature.

Oxygen, which appears in close environment around steel in the presence of water, consumes electrons and transforms into the OH^- ions. The cathodic reactions take place:



Under the OH^- presence, the iron hydroxide forms. That compound is a relatively soluble in aqueous media and may form oxides or different hydroxides, dependently on the pH of the environment. Concrete has high pH, which results in the formation of a passive layer of Fe_2O_3 around steel. Concrete under the physical and thermal stress is permeable to water, oxygen from the air and different ions, what results in further corrosion and formation of pits. General overview on the pitting corrosion has been presented on the picture 1.

3. Corrosion inhibition in concrete

Corrosion inhibitors may be divided into groups, depending on their mechanism of protection against corrosion, environment, protection layer and type of structure and composition or their physicochemical properties. Total inhibition of corrosion is almost impossible, however the use of inhibitors enables to limit the process' speed and aggressiveness. Due to the ecological constraints inorganic inhibitors are frequently replaced by compounds less harmful to environment. In this paper we focused only on the inhibition of corrosion by organic compounds. Corrosion is based mostly on the electrochemical mechanism, in which metal dissolves into the solution through the electrons flow. The site of metal dissolution acts as an anode and acceptor area in metal where electrons flow acts as a cathode. Anodic process corresponds to the oxidation by the dissolution of metal and cathodic reaction is the reduction process where oxygen dissolved in water forms OH^- ions. Transfer of electrons from anode to cathode is possible by the formation of pores in concrete.

Anodic and cathodic reactions taking place during corrosion are named half-cell reactions. Steel under corrosion works as connected electrodes: the anode and the cathode. Water presented in concrete works as an electrolyte solution in pores. Based on the electrochemical character of reactions the potential of electrode can be derived by the general reaction (14) and considering by the Nernst equation (15):



$$E = E^0 - \frac{RT}{nF} \ln \left(\frac{[a_M]}{[a_{M^{n+}}]} \right) \quad (15)$$

In case of the iron electrode the reaction (16) can be derived by anodic equation (17) (Ahmad 2003):



$$E_A = -0.441 - \frac{RT}{2F} \ln \left(\frac{1}{[Fe^{2+}]} \right) \quad (17)$$

Due to the cathodic reaction (12) the Nernst equation is described by (18).

$$E_C = -0.40 + \frac{RT}{4F} \ln \left(\frac{[O_2][H_2O]}{[OH^-]^4} \right) \quad (18)$$

For iron in the concrete the reaction includes also the oxygen presence:

$$E = 1.669 + 0.0418 \log[O_2] - 0.059 pH - 0.0269 \log[Fe^{2+}] \quad (19)$$

The equation indicates that the rate of corrosion is affected by many factors like: $[O_2]$ concentration of oxygen in concrete (oxygen availability), $[Fe^{2+}]$ concentration of ferrous ions in concrete near the rebars and the pH of electrolyte in concrete (while pH varies under the carbonation process).

Where $[O_2]$ is the concentration of oxygen and $[Fe^{2+}]$ is the concentration of iron ions in concrete located near the reinforcement.

Those electrochemical reactions can be delayed by the formation of a passive film or reduction of corrosion rate after depassivation. Organic inhibitors can delay anodic, cathodic or both types of reactions. For anodic

inhibition of corrosion calcium nitrates are often used to increase the potential of steel. For cathodic inhibition, the pH of steel environment is increased through the application of alkali compounds. In comparison to the anodic and cathodic inhibition, mixed inhibition does not require a significant change of corrosion potential. In mixed corrosion inhibition steel is frequently covered by protective organic layer with polar groups such as $-\text{NH}_2$, $-\text{SH}$, $-\text{COOH}$, $-\text{SO}_3\text{H}$ or OH . In this paper only organic inhibitors are discussed.

3.1. Organic inhibitors

Among many available methods of efficient protection of rebars in concrete against corrosion the application of organic inhibitors is attractive due to their properties, low cost and availability in the market. Organic inhibitors can be used as admixture corrosion inhibitors (ACI) (Hansson 1998; Gaidis 2004; Angst et al. 2016), added directly into the freshly mixed concrete or migrating corrosion inhibitors (MCI) (Gaidis 2004; Ormlisse et al. 2007), which are able to penetrate into the concrete after their application onto the concrete surface.

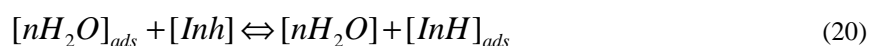
The effectiveness of the corrosion inhibitors lays in their chemical structure. Due to the high compression on the metal and wide area occupied on metal, the organic corrosion inhibitors may screen iron atoms in the steel with a protective barrier film (Sanyal 1981). Both, ACIs and MCIs are able to create the thin layer on the rebars preventing against corrosion, however the mechanism of the corrosion inhibition is mainly influenced by the chemical structure of the compound used. It was described that chemical structure is a significant factor with organic inhibition. Inhibitive properties depend on the electron density of hetero-atoms like nitrogen, oxygen, sulfur and phosphorus, molecular size and type of adsorption with metal surface (Dariva and Galio 2014). Presence of the nitrogen atom in compounds like amines or alkanolamines (aminoalcohols) influences the effectiveness of inhibition (Batis 2003; Ormlisse et al. 2006; Ormlisse et al. 2010). For organic inhibition by a protective barrier film formation on the steel also organic salts of mentioned compounds can be used. Heteroatoms influence the inhibitive properties of organic compounds. The efficiency of inhibition is the highest for phosphorus and decreases in the following order: $\text{P} > \text{S} > \text{N} > \text{O}$ (Papavinasam 2000). Amines, alkanolamines and their salts are typically used as organic inhibitors of corrosion in concrete (Wombacher et al. 2004; Mechmeche et al. 2008).

Amines and alkanolamines, similarly to ammonia (NH_3), contain basic nitrogen atoms with a lone electron pair ($\text{N}:$) in their molecules. Lone electrons present in nitrogen influence the shape of the molecule. Due to the lone electron pair, the structure of amines resembles that of ammonia in their trigonal pyramide geometrical shape, with electrons occupying the fourth corner. Amines are organic derivatives of ammonia (NH_3) with a general formula of NR_3 , where R may be hydrogen (H) or, alkyl or aryl group. Like ammonia, they contain in their molecules a basic nitrogen atom with a lone electrons pair ($\text{N}:$) – this makes amines organic bases and polar molecules. Due to the lone electron pair and polar character of such compounds they are regarded as reaction centers of adsorption process and effective inhibitors of the active sites of corrosion on metal surfaces. Amines are widely used as corrosion inhibitors (Söylev et al. 2007a; Söylev et al. 2007b; Mechmeche et al. 2008; Xu et al. 2016), however those compounds are also functionalized by different functional groups to protect steel against corrosion more efficiently. Alkanolamines (aminoalcohols) contain both functional groups an amine and alcohol. Aminoalcohols, analogically to amines, have been claimed to be good protectors of rebars against corrosion (Shi and Sun 2012; Liu et al. 2016), however some studies have shown the delay of the corrosion, not the reduction of already started corrosion rate (Kern and Landolt 2001; Bolzoni et al. 2006; Rakanta et al. 2013; Vyrides et al. 2013). Song and Saraswathy (2007) reported alkanolamines as corrosion inhibitors, showing the influence of the alkyl chain on the inhibitive properties of such compounds. In that studies triethanolamine protects steel against corrosion in concrete more than monoethanolamine. Morris et al. (2003) have shown that aminoalcohols can be used as efficient inhibitors, however their inhibitive properties changes under the changes of chlorides content in concrete. Aminoalcohols decreases corrosion by attacking cathodic sites on steel where oxygen picks up electrons and is reduced to OH^- ions. Aminoalcohols are also able to adsorb on the anodic sites of the steel surface (Gaidis 2004).

Organic inhibitors can adsorb by chemisorption or physisorption. Chemisorption includes the charge transfer between heteroatoms and iron surface or sharing of the charge to create the coordinate bond. Physisorption of organic compounds on steel involves electrostatic interactions between charges of dipoles of organic molecules and the charge of the rebars' metal surface. Inhibitors absorbed on the metal surface via heteroatoms block the active sites with their polar groups and subsequently decrease the corrosion rates (Ahmad 2006). It was found

that functional groups like amine group or -O, -SH, -SO₃H, -COOH are chelating agents and are able to form chelate rings. Donor groups, like the amine group, adsorb onto the steel with their lone electron pair. They donate electrons to the iron ions on the metal surface, which behaves as a Lewis's acid (Ormellese et al. 2009).

Chemisorption leads to the chemical reaction between active centers of corrosion onto metal and organic inhibitor, where charges from the polar group of inhibitor and charges from metal and metal oxides formed in concrete are shared. Then organic inhibitor forms the thin coating film blocking the metal surface from the aggressive species by strong chemical bonds. Physisorption leads to the formation of mechanical barrier, made by organic inhibitors. That type of adsorption prevents the metal from the ionic species from environment and ionic species from dissolved metal. Adsorbed molecules with lone electron pairs or ones that are negatively charged repulse the chloride ions (Ormellese et al. 2010). Physisorption is based mostly on the electrostatic attraction between metal surface, metal oxides and polar groups from inhibitor. The strength of adsorption depends on the charge on the functional group with loosely bound electrons, conjugated π -bond system in chain or aromatic ring. Corrosion undergoes faster when the water adsorb on the metal. Due to the process of physisorption, organic inhibitors replace the water on the metal surface due to the reaction (20). The ability of organic inhibitor to replace water depends on electrostatic interactions between inhibitor and metal, and orientation of inhibitor structure.



Tertiary amines have higher ability to protect steel against corrosion compared to secondary or primary amines. Their ability to inhibit the corrosion based on their molecular structure. Polar N atom with lone electron pair forms the bond with corroding metal. Delocalized electrons from the aromatic groups connected with nitrogen atom increase the inhibitive properties of such compounds by inductive effect. The raise of amine structure size also increases the inhibition property by steric effect. Compounds with bigger structures form layers less permeable for aggressive species than small compounds do (Fei et al. 2014). Aromatic compounds with π -bonds exhibit the most effective and efficient inhibitive properties. That effect comes from an interaction of the active metal surface with π -orbitals from the aromatic inhibitor. The same effect has been observed with elongation of the chain in aliphatic amines. Non-polar hydrophobic groups position perpendicularly to the steel surface acting as barrier and repelling aggressive environmental species. The rate of corrosion decreases with the elongation of amines chain. In concrete steel undergoes corrosion, when the pH decreases. Addition of amines leads to the bonding the hydrogen from water on the metal surface. In this way water is desorbed and chemisorbed by amines. Through this chemical bonding of water, amines are also physisorbed on the metal surface and form a protective barrier layer, due to the reaction (21) and Figure 2.

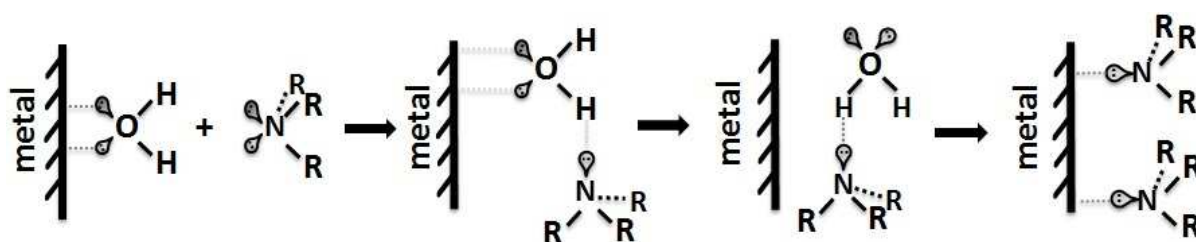


Fig. 2. Schematic picture of reaction (21).

When the organic inhibitor is added to the system the hydrophobic group from the polar compound orients itself perpendicularly to the metal surface and blocks aggressive corrosive fluids. Aggregated hydrophobic groups form a tight barrier and create an impermeable layer for chloride ingress into the concrete. In comparison to amines and alcoholamines compounds containing in their structure O, S or P are also good corrosion inhibitors in alkali media. Carboxylic acids have polar groups, where oxygen contains lone electron pairs, able to bond chemically and physically. They form carboxylate anions, which are able to adsorb on the surface of steel. In contrast to amine groups, carboxylic groups act as proton donors and are considered Brønsted-Lowry acids (Ormellese et al. 2009). Carboxylates adsorb on the metal surface through the ionic form of carboxylic group

-COO⁻ group adsorbs on the metal by electrical charge delocalized on the oxygen atoms in the -COOH group. It was found that that inductive and resonance effects on the electron density of the molecule influences the adsorption of organic inhibitors on the steel, see Figure 3.

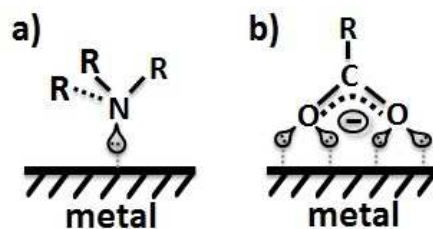


Fig. 3. Scheme of functional groups a) amines, b) carboxylates on the metal surface.

Other group of compounds used as organic inhibitors are aminoacids, containing in their structure amine and carboxylic groups. Mechanism of inhibition of corrosion has not been yet explained sufficiently. Among many theories of corrosion inhibition adsorption of organic compounds and formation of barrier layer seems to be the best explanation of amines and alkanolamines effect of protection against corrosion. Amines and alkanolamines adsorb on the metal surface and form a protective film against corrosive species like chloride ions (Monticelli et al. 2000; Monteiro et al. 2015; Liu et al. 2016). As well as amines, the carboxylates molecular structure is strongly linked with the inhibition of corrosion (Myrdal 2010). Due to the inductive effect of functional groups connected with the -COO⁻ the electrostatic repulsion towards chloride ions occurs (Cabrini 2015). Inductive effect changes with the electronegativity of the groups and raise of the carbon chain length and simultaneous steric effect leads to the better inhibition against corrosion. Functional groups linked with -COO⁻ are not directly involved into the adsorption, however they are responsible for electrostatic repulsions. Adsorption is observed for the -COOH⁻ group interacting with the metal surface. Alkyl chains, as well as other substituents, form a good physical barrier against chloride ions if the steric effect is large. Presence of two or more relatively closed located in the molecule carboxylate groups improve inhibitive properties. That enables to complex not only ferrous, but also ferric species competing with chloride ions (Sagoe-Crentsil et al. 1993).

In spite of the electrostatic character of inhibition towards chloride ions and steric effect of functional groups in carboxylates, this type of compounds are able to form complexes due to the chelation process. Carboxylates (mono- and polycarboxylates) are also the best corrosion inhibitors among amines and alkanolamines, see Figure 4 (Ormellese et al. 2009).

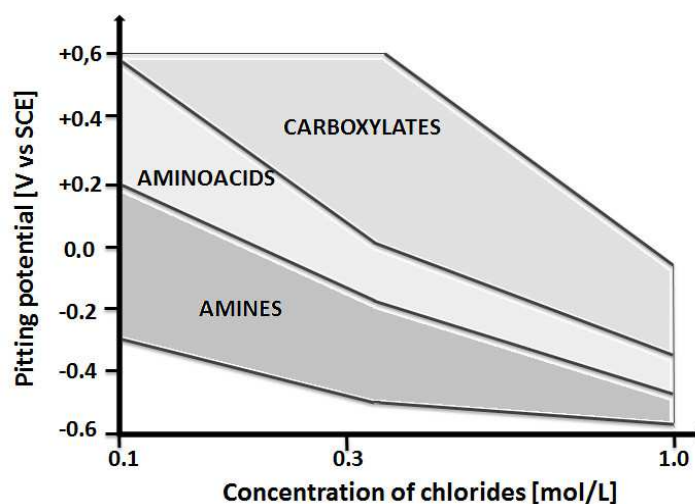


Fig. 4. Schematic Pedeferrri type diagram showing pitting potential as a function of chloride ions and the range of corrosion organic inhibitors (Ormellese et al. 2009).

Various reports and paper describes many different organic inhibitors of corrosion, however among them the most popular based on the amines and alkanolamines. Such compounds have been considered as efficient

inhibitors, due to their structural properties (Jamil et al. 2003; Jamil et al. 2004). Despite of the broad application of amines, alkanolamines and carboxylates in the rebars corrosion inhibition in concrete it is shown that still many problems must be solved regarding their effecting inhibition effects. In literature that other organic compounds have been reported as efficient corrosion inhibitors. Among different organic inhibitors of corrosion the Multi-Functional Organic Inhibitors (MFOI) are described as efficient corrosion inhibitors (Nmai 2004). MFOI consist of amines and fatty-acid esters and provide a twofold mechanism of corrosion inhibition. Due to their chemical structure they form a protective film onto the corroding metal surface blocking chloride ions. At the first stage in alkali media, like concrete, esters are hydrolyzed and form alcohol and carboxylic acid, which carboxylic ion quickly reacts with calcium ion and forms the coating. The fatty-acid esters arranges on the rebars and chain the non-polar groups forming tight, mechanical barrier (called film-forming amine component FFA) non-permeable for moisture, oxygen and chloride ions. Additionally MFOIs act as chelates. Due to the polar groups in the molecules they are able to form six-membered chelate rings.

Organic compounds added as admixtures reduce permeability of concrete. Benzotriazoles (Ababneh et al. 2012), benzotriazole derivatives (Sheban et al. 2007; Monticelli et al. 2002), and azoles (Subramaryam et al. 1985) containing tertiary amine groups in the ring form strong bond with the metal surface in alkali media. Benzotriazoles and their derivatives operate as good inhibitors against chlorides attack in concrete. Some studies have shown that substituents in benzotriazoles have significant effect on the inhibitive properties of those groups of organic inhibitors. Shi and Sun (2012) reported that benzotriazole (BTA) exhibit higher inhibitive properties than inorganic inhibitors in order: BTA > NaNO₂ > Na₃PO₄. It was also reported that BTA can be used as mixed inhibitor (Shi and Sun 2012). Application of electron acceptors like -Cl group improve inhibition efficiency, while donor group like -NO₂ have opposite effect. Inhibition efficiency decreases in order: 5-chlorobenzotriazole > benzotriazole > 5-nitrobenzotriazole (Abd El Haleem et al. 2014). Organic alcohols like ascorbic acid (Valek et al. 2007) or aromatic amines with various functional groups (tiophene, carbonitrile) (Gürten et al. 2007; Ameer et al. 2010), tested in alkali solution adsorb effectively on the metal surface and form a barrier preventing from chloride ions and act as efficient corrosion inhibitors. Some studies show that compounds like calcium palmitate and their combinations with calcium nitrate also enable the inhibition of corrosion in concrete (Kumar et al. 2013). Sodium gluconate can also adsorb onto the reformed metal with the final formation of a chelating layer which delays the chloride ions attack (Li et al. 2015). Another group of compounds investigated as corrosion inhibitors in concrete are emulsions of saturated fatty acids (Bolzoni et al. 2005). Szauer and Brandt (1985) were also tested amine salts of fatty acids as corrosion inhibitors on iron. Besides organic compounds based on the nitrogen and oxygen, Etteyeb et al. (2015; 2016) have applied phenyl phosphonic acid as effective corrosion inhibitor forming complexes with iron on the top of steel rebars. Monticelli et al. (2002; 2011) have described influence of 2-amino-benzoate and glycerol-phosphate on the corrosion of steel in concrete. Diamanti et al. (2015) reported application of tartrate, benzoate, glutamate and amines, where among various compounds tartrate maintained the best inhibitive properties. β-glycerophosphate has been found as promising candidate for application in concrete as admixture with inorganic salts (Yang et al. 2008). Due to the growing need for corrosion inhibition of rebars in concrete, every year new materials, even natural corrosion inhibitors are tested as corrosion inhibitors (Raja et al. 2015; Kundu et al. 2016; Raja et al. 2016). Other group of compounds applied as corrosion inhibitors are amino-esters (Ormellese et al. 2006). They are used as admixtures reducing the corrosion process (Al Zubaidy and Al Tamaimi 2012; Saraswathy et al. 2013). Analogically to amino-esters, carboxylate esters hydrolyzed to the alcohol and insoluble calcium salt with hydrophobic alkyl chain, blocking the pores in concrete (Gaidis 2004). Among various parameters the content of organic inhibitor in concrete plays crucial role (Morris and Vazquez 2002; Rakanta et al. 2006).

3.2. Side effects

Organic corrosion inhibitors are admixtures which can do more than just inhibit corrosion of steel (Table 1; other side effects on the fresh and hardened concrete properties are reported to be negligible). Chemical additives can significantly affect the physical and mechanical properties of cement because of their physical and chemical interactions with hydrates and/or unhydrated phases. Aminoalcohols have been used as additives in cement production and concrete technology for many years. For instance, triethanolamine (TEA), a tertiary alkanolamine, is well-known as a multifunctional chemical admixture for concrete and an effective grinding aid for cement manufacturing (in order to prevent agglomeration of powder and coating formation on milling ball

surface). Depending on the cement type and dosage, TEA can produce either set acceleration or retardation of cement hydration. An addition rate of 0.02% to the type I Portland cement, TEA acts as a set accelerator, at 0.25% as a mild set retarder and at 0.5% a severe retarder and at 1% a very strong accelerator. The effect on the strength development in cement pastes is also dependent on the added amount of TEA (Aggoun et al. 2008). The present economic constraints require acceleration in the speed of work in the construction industry. The need for a concrete with sufficient strength at a very early age (caused by accelerating admixture like TEA) is in many situations very important. An additional advantage of using TEA can be corrosion inhibition.

Table 1. The side effects of the organic inhibitors.

Properties	Effects
odor of cement composites	possible ammoniacal (amines)
setting and early-strength development of concrete	can accelerate or retard, it depends on type and concentration of organic inhibitor (Han et al. 2015; Dodson et al. 1990)
air content	no significant effect but inhibitor sometimes required increasing the amount of air entraining admixture to achieve a given air content (Nmai et al. 2004)
viscosity	organic corrosion inhibitors reduce viscosity of self-compacting concrete (Blankson and Erdem 2015)
permeability	it depends on type of organic inhibitor (for instance, organic acids react with cement components or hydration products - pore blocking effect (Söylev et al. 2007b))
workability	it depends on functional groups (De Schutter and Luo 2004), inhibitors with groups like -OH and -COOH causes an increase of workability; other inhibitor sometimes required additional superplasticizer to achieve the desired slump (Söylev et al. 2008)
steel-concrete bond	possible reduction of adhesion between steel and concrete (Söylev et al. 2007b)

4. Conclusions

Steel in concrete is passive and protected by oxy-hydroxy layer due to the high alkalinity of concrete promoting inhibition. Unfortunately, corrosion occurs even on passive state-steel, and is vastly exacerbated when concrete loses its protective properties. Concrete is a porous material, so corrosion is accelerated by the penetration of aggressive ions like chloride or decrease of pH of the solution inside pores, especially under the concrete carbonation. Once the pitting corrosion is initiated, the cathodic protection by organic inhibitors can be used to control the corrosion rate. In general, organic inhibitors change the potential between steel and solution in the pores of concrete or create a mechanical barrier against aggressive ions.

Inhibition properties of organic molecules and inhibition efficiency depend on many factors (Mann et al. 1936; Costa and Lluch 1984; Vosta and Eliasek 1997; Papavinasam 2000; Khalil 2003; Ormellese et al. 2009), however the main can be considered as:

- length of the alkyl (carbon) chain,
- aromaticity (ring system) or conjugated (π -bonding),
- structure of chemical compounds and the steric effect (shape and volumetric size of molecule),
- type of polar functional groups and bonding atoms,
- position of substituents in the polar groups,
- nature of substituent groups, the induction effect (charge shift on the polar, functional group) or resonance effect (charge delocalization in molecule),
- electrostatic effect,
- number of bonding atoms,
- number of polar groups,
- type of interactions between organic inhibitors and metal surface,
- concentration of inhibitors,
- charges density on the metal surface,
- charges density on the organic inhibitor,
- molecular orbitals of the applied compound,
- dipole moments,
- ability for a layer to become cross-linked or compact.

Inhibition efficiency is also influenced by other factors like:

- composition of concrete and its pH,
- concrete porosity,
- availability of oxygen,
- temperature,
- concentration and type of aggressive ions in concrete.

The most effective corrosion inhibitors contain π -bonds in their structure, due to the π -orbitals from organic compounds interacting with electrons in the metal. The polar groups with S, O or N atoms are needed to allow adsorption on the active corrosion sites and metal surface blockade. The most effective substances in inhibition against corrosion are: amines, aminoacids and carboxylates (Bolzoni et al. 2005). Generally, the alkyl chains or voluminous substituent groups form a physical barrier protecting the steel surface against chloride attack. Inhibition is more efficient when the organic compound adsorbs onto the γ -FeOOH, which is crucial for efficient inhibition against corrosion.

The inhibition properties decreases in order: carboxylates > aminoacids > amines (Bolzoni et al. 2014). Effective organic inhibitors decreases corrosion rate of the anodic regions in rebars, decreases the probability of corrosion by increase of the corrosion potential and increase of electrical resistivity in the anodic region covered by organic inhibitor. Organic inhibitors may contain single or multiple functional groups like: -OH, -C-O-C-, -COOH, -CONH₂, -SH, -C-N-C-, -NH, -NO₂, -N=N-N-, -S-, -S=O, -C=S-, -P=O, -P-, -As-, -Se-, however many of them only delay the corrosion of the embedded steel exposed to chloride and carbonation. Therefore, there is need for more research about the application of organic inhibitors in the building industry.

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