Inhibitor evaluation in different simulated concrete pore solution for the protection of steel rebars

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HIGHLIGHTS

- Determination of 3 critical situations in which the corrosion inhibitor should act.
- The green inhibitor Na_2MoO_4 can inhibit both pitting and uniform corrosion.
- Thanks to its specific inhibitor mechanism molybdate can prolong the service life.

ARTICLE INFO

ABSTRACT

Corrosion of reinforcement steel forms a huge problem worldwide. A possible remedy for this problem is the application of corrosion inhibitors. The purpose of this research is to evaluate different inhibitors for both types of corrosion that can occur in reinforced concrete: pitting corrosion (by chloride attack), and uniform corrosion (by a drop in pH). Potentiodynamic polarization measurements in realistic concrete pore solutions (CPS) revealed three critical situations — representing pitting and uniform corrosion, and the combination — in which the inhibitor needs to act. According to polarization experiments and micrographs Na_2MoO_4 is the best performing inhibitor for the three cases. Our XPS measurements are in line with the proposed inhibitor mechanism by Vukasovich (1986), which is very complex and depends on whether the surface is active or passive to start with. In conclusion Na_2MoO_4 is a possible — and environmental-friendly — candidate to prevent corrosion of reinforcement steel.

1. Introduction

Reinforced concrete is one of the most commonly used building materials. The steel rebars provide a higher tensile strength and/or ductility to the concrete, but their susceptibility to corrosion can jeopardize the durability of the concrete structure. Worldwide corrosion of steel reinforcement is a huge problem as the premature failure of concrete structures leads to safety issues and entails an enormous cost for repair and replacements.

In an alkaline environment like concrete (pH > 10) steel is normally passivated. However, there are two main reasons that cause the passive layer to break down. On the one hand, ingress of aggressive ions (e.g. chloride ions) can cause the localized breakdown of the passive film leading to pitting corrosion. On the other hand, carbonation leads to a decrease in pH — when it drops below 10 no stable passive layer can be maintained — hence uniform corrosion can take place.

One method to avoid/limit corrosion of reinforcement bars is the use of corrosion inhibitors. Corrosion inhibitors are defined as chemical compounds that decrease the corrosiveness of a certain environment when present (even) in relatively low concentrations. Different inhibitor mechanisms are known; for example, certain inhibitors eliminate a chemically active substance from the environment (e.g. removal of dissolved oxygen) by reacting with it, other inhibitors form a thin protective layer [2]. Depending on where the inhibitors act a distinction can be made between anodic inhibitors, which impede the oxidation reaction, cathodic inhibitors, which decrease the reduction reaction, or mixed inhibitors which act on both half-reactions. Consequently, the inhibition effectiveness depends on the corrosive environment and the metal surface it needs to act on. [2].

Inhibitors can be applied either preventively, which is mainly done by addition to the mixing water of fresh concrete, or restoratively as a surface applied inhibitor after the concrete has hardened [3–5]. Most commonly used inhibitors are nitrites (calcium nitrite

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and sodium nitrite) and various organic inhibitors such as aminoalcohols and amines (in some cases blends are also used); as surface applied inhibitor sodium monofluorophosphate (MFP) is also regularly used [3–11]. Additionally molybdate, tungstate, chromate and other phosphate anions have already been tested for their anti-corrosion properties [12–15].

Unfortunately there are some drawbacks when using inhibitors that have to be taken into account. First of all, toxicity can limit their use in practical applications. The use of sodium chromate, for example, is prohibited by EU directives (REACH) as it is listed as carcinogenic, mutagen and toxic for reproduction [16]. Secondly, certain interactions between the inhibitor and concrete components can take place, influencing the concrete properties (which can turn out positively or negatively) [4,17], or leading to inhibitor deactivation, e.g. when mixing in MFP in fresh concrete the active component PO_3F^- reacts with the calcium ion to form insoluble products [3]. Finally, a certain threshold concentration of the inhibitor (with respect to the concentration of aggressive ions) always needs to be present — locally — at the steel surface to assure effective inhibition. If the present inhibitor's concentration is too low, the risk exists that the corrosion process will even be accelerated [3,4]. This is especially the case for surface applied corrosion inhibitors, since getting a sufficient concentration of inhibitor to the rebar intrinsically entails a challenge. Furthermore, also for the admixed inhibitors it can be a difficult requirement in the long term because the inhibitors can be washed away or evaporate. For both forms of application this also means that only a (small) percentage of the introduced inhibitor is used efficiently.

The idea of our research is to incorporate a non-toxic and environmental-friendly corrosion inhibitor in a coating on the rebar, such that there can be a controlled release of the inhibitor when necessary, directly to the rebar, for efficient corrosion protection. This paper presents the first step in our research: selecting the best-performing inhibitor out of five different organic and inorganic inhibitors in a simulated concrete pore solution (CPS).

In general, researchers try to find corrosion inhibitors that can either prevent pitting corrosion (by chloride attack) [10,11,14,15] or uniform corrosion (due to carbonation) [12,13], but the combination of both causes of corrosion — which is most likely to occur in practice — is rarely considered. Furthermore most of these studies are performed in a saturated $Ca(OH)_2$ solution, which according to Poursaee, "does not represent a realistic concrete environment" [18]. Indeed, in practice the composition of a concrete pore solution is much more complex, because also other components can have an influence on the electrochemical behavior of steel and/or on the inhibition action of a certain corrosion inhibitor. Therefore we chose to evaluate the corrosion inhibitors in two *realistic* concrete pore solutions which represent the two different types of corrosion that can occur. On the one hand, a highly alkaline CPS containing chlorides simulating the pitting corrosion, on the other hand a carbonated CPS with pH < 10 mimicking a situation of uniform corrosion. Additionally the combination, a carbonated CPS with chlorides, is tested. In literature one can find numerous articles on "the" chloride threshold value (or "the critical chloride content"), but this topic leads to considerable discussions and controversy [19]. The reason for this is because there is no unique chloride threshold; it depends in the first place on which definition is considered and additionally its value depends on several influencing parameters (e.g. the experimental procedure to determine it) [19–21]. Hence we decided to determine the critical situations for our specific cases, i.e. the realistic concrete pore solutions we used. In those situations the inhibitors sodium molybdate (Na_2MoO_4), cerium nitrate ($Ce(NO_3)_3$), 2,5-dimercapto-1,3,4-thiadiazole (DT), 2-mercaptobenzothiazole (MBT), and 1H-benzotriazole (BTA) were then examined.

2. Materials and methods

2.1. Steel

All the steel samples used in this research are Q-panel type S substrates. Steel plates were chosen over steel reinforcement bars as plates have the advantage they allow for easier electrochemical measurements and especially easier surface analysis, which in this study is of utmost importance. Moreover we believe that the expected reactions on both steel surfaces are comparable, and thus the plates are representative for the reinforcement bars. Before use the samples are cleaned with ethanol and rinsed with Milli-Q water.

2.2. Simulated concrete pore solutions

The idea of the different concrete pore solutions is partly based on the article of Moreno et al., describing the effect of carbonation and chloride content on the corrosion of reinforcing steel [22]. However the exact — more realistic — compositions of the solutions are chosen such that the ions that are present fall within the range of values that were found in real concrete pore solutions [23].

To mimic the situation of pitting corrosion a CPS with pH 13 was prepared by mixing potassium hydroxide (KOH, 0.3 M), sodium hydroxide (NaOH, 0.1 M), calcium hydroxide ($Ca(OH)_2$, 0.01 M), and sodium sulphate ($NaSO_4$, 0.002 M). Then 0; 0.5; 1; 2; and 5 wt% Cl^- was added, which means respectively a concentration of 0; 0.14; 0.28; 0.56; 1.4 M NaCl. In the rest of the article we refer to this CPS as $CPS_{x\%Cl^-}$.

A carbonated CPS in which uniform corrosion can take place is simulated by mixing calcium carbonate ($CaCO_3$, 0.001 M) and sodium sulphate ($NaSO_4$, 0.002 M). This CPS is named CPS_{carb} and has a pH of 9.

Last also the combination of carbonation and chloride attack — the "worst case scenario" — is prepared by adding 0.0.014 M NaCl to the CPS_{carb}. The result is $CPS_{carb+0.05\%Cl^-}$, also with pH 9.

The pH of the solutions was verified with a inoLab pH meter from WTW GmbH.

2.3. Inhibitors

The following inhibitors were used:

- Sodium molybdate dihydrate ($Na_2MoO_4 \cdot 2H_2O$) with a purity $\geqslant 99.0\%$, obtained from UCB;
- Cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$) with a purity = 99.0%, obtained from Aldrich;
- 2,5-Dimercapto-1,3,4-thiadiazole (DT) with a purity $\geqslant 98.0\%$, obtained from Merck KGaA;
- 2-Mercaptobenzothiazole (MBT) with a purity $\geqslant 97.0\%$, obtained from Merck KGaA;
- 1H-benzotriazole (BTA) with a purity $\geqslant 98.0\%$, obtained from Fluka.

All the inhibitors were used as received. To evaluate the corrosion inhibitors a concentration of 10^{-4} M was used in the respective concrete pore solutions. This relatively low concentration is considered to be representative for the actual concentration of inhibitor that can be present in a practical application.

The above mentioned inhibitors are not restricted in their use by REACH, and none of them is identified as carcinogenic by IARC. However MBT may cause an allergic skin reaction, DT and BTA may cause serious eye irritation, and $Ce(NO_3)_3$ even serious eye damage. Up to now there are no indications that Na_2MoO_4 is harmful or toxic for human life. Further, considering the ecological