EFFECTIVENESS OF MIGRATORY CORROSION INHIBITORS IN SIMULATED PORE WATER OF CHLORIDE-CONTAMINATED CONCRETE BY MEANS OF ELECTROCHEMICAL TECHNIQUES

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Abstract

Corrosion of steel in concrete is the major cause of premature deterioration of reinforced concrete structures. Various methods to improve the durability and extend the service life of concrete structures have been used for the past two decades. More recently, migrating corrosion inhibitors (MCI) are found to be one of the most simple and effective methods to control rebar corrosion in concrete structures. This study was performed to test the inhibition properties of amino-alcohol and amine-carboxylates based corrosion inhibitors in solutions of simulating the concrete pore water and thus to develop curative inhibitor. The results show that the monoamine-carboxylate inhibitor was inefficient when it was used in the conditions of chloride contamination solution and only the ternary amine-carboxylates inhibitor showed an acceptable inhibitive action. The linear polarization resistance and potentiodynamic scanning curves show that the curative inhibitor is not only able to effectively decrease the corrosion rate of the steel electrode in chloride containing environment but has a excellent self-repairing ability even when the steel is under strong anodic polarization. The test of integrative effect with surfactant addition in the curative inhibitor further indicate that the inhibition properties have great increase in Ca(OH)2 solution with 1-3% NaCl. The electrochemical impedance spectroscopy (EIS) fitting data suggest that the protective layer of the curative inhibitor at the surface of steel becomes homogeneous and compact in presence of chloride. The results in this work help to fill some doubts on the performance of organic inhibitors and help to develop a curative inhibitor.

Keywords: migratory corrosion inhibitors, simulated pore solutions, concrete contaminated with chloride, electrochemical techniques
1. INTRODUCTION

Reinforced steel in concrete are normally passivated due to a passive film is formed at the surface of steel in cement high alkalinity condition and the steel is free of corrosion. However, when the pH value of solution around the steel surface drops below 9.0 due to carbonation of concrete or leaching of calcium hydroxide (CH) during the service period, the passive film may be destroyed and corrosion initiates. In addition, chloride ions are another major factor of promoting steel corrosion in concrete. In case the concentration of chloride ions at the steel surface exceeds the threshold, the local breakdown of the passive film and corrosion may occur. For reinforced concrete structure in normal environmental condition, using high quality concrete and adequate cover are normally sufficient to prevent corrosion. But for concrete in severe environmental conditions or structure using de-icing salt in winter, additional prevention methods have to be used. The methods include surface coatings of concrete, utilization of epoxy coated steel bar, desalination, cathodic protection, addition of inhibitive admixtures, etc. As for old concrete structure, migrating corrosion inhibitors (MCI) are found to be one of the most simple and attractive methods to control rebar corrosion in concrete structure [1-7]. The commonly used MCIs are a mixtures of alkanol amines and amines or alternatively organic acids, which are able to penetrate through the capillary pores and micro cracks of the concrete structure [2,3,7]. The inhibition abilities of the MCI have been widely studied. However, the results found in the literature are sometimes contradictory. Some authors [1,5] reported that the inhibitors are effective in reducing corrosion rate in concrete contaminated with chlorides while others report that they are not effective when chloride content in concrete is higher than 0.43% [6]. Very little is known about the work mechanism by which they lead to increased corrosion protection and how to improve the curative property in high chloride conditions. The aim of this work is to test the inhibition effect of amino alcohol based inhibitors and to develop a self-healing inhibitor in solutions of simulating the chloride-contaminated concrete pore water. This paper partially presents the results from electrochemical tests, relevant to the steel surface.

2. EXPERIMENTAL METHODS

Tests were carried out in solutions of simulating different states of the pores electrolyte in the concrete with or without chloride. The practical procedures have been chosen to simulate two different modes of use: preventive and curative. The solution of simulating chloride-contaminated concrete pore water were made by mixing NaCl with pellucid saturated Ca(OH)₂ (CH) solution (pH about 12.5). The NaCl concentration was kept at 0.4% (4g/l), 1% (10g/l) and 3% (30g/l) of the CH solution. The proportions of inhibitors are from the minimum i.e. 0.4% (4g/l) to the maximum i.e. 4.38% (43.8g/l) accordingly. The solution was slowly agitated and maintained around 20°C. Tested steel specimens were cut and machined from commercial re-bars used for concrete reinforcement. Each specimen circumference was masked with epoxy resin to leave one exposed end (ground down to grade 1000 by emery paper). The area exposed to the solution was approximately 1.00cm². The steel electrode was welded to a copper wire in order to ensure electrical contacts for electrochemical tests. Their cross section surfaces were polished with emery paper and degreased in ethanol then rinsed with distilled water before testing. In order to evaluate the action of the inhibitor, different electrochemical tests were performed in a three-electrode cell. Saturated calomel electrode (SCE) and platinum foil were used as reference and auxiliary electrodes, respectively. Free
corrosion potential ($E_{corr}$) was monitored with respect to SCE reference electrode. Linear Polarization Resistance (LPR) measurements and electrochemical impedance spectroscopy (EIS) were used to detect the corrosion behavior of the steel specimens. The specimens were additionally investigated by potentiodynamic polarization tests. All electrochemical tests were performed using Princeton Potentiostat (273A). The Impedance data were obtained at corrosion potential with a perturbing signal of ±10 mV, using a 5210EC Two Phase Lock-in Amplifier connected to the Potentiostat. The frequency span was from 100 kHz to 0.1 Hz. The experiment and registration of data were conducted under computer control using the software PowerSUITE. Fitting of the data was done using the EIS modeling software of ZsimpWin. LPR values were determined by polarisation tests with a scan rate of 10 mV/min, from -10 mV to +10 mV with respect to $E_{corr}$. Corrosion rate was calculated by the formula: $i_{corr} = B/R_p$. The proportionality constant $B$, for a particular system can be determined empirically, as shown by Stern and Geary equation, can be calculated from $b_a$ and $b_c$, the slopes of the anodic and cathodic Tafel slopes, i.e. $B = b_a\cdot b_c/2.3(b_a+b_c)$.

3. RESULTS AND DISCUSSION

3.1 The preventive effect of inhibitors addition

Fig.1 depicts the corrosion current ($\mu A/cm^2$) of the steel electrodes in Ca(OH)$_2$ solution contaminated with 0.4% NaCl with and without inhibitors addition. The three inhibitors are unitary, binary and ternary amine-carboxylates prepared in laboratory respectively. The tests prove that the addition of amine-carboxylates inhibitors in the solution decrease the corrosion currents effectively, especially the addition of ternary amine-carboxylates decrease the corrosion currents by about two orders of magnitude. That indicates the corrosion reactions are strongly hindered at the initial hours after mixing. Fig.2 shows the changes of linear polarization resistance (Ohm.cm$^2$) of the steel electrode in saturated Ca(OH)$_2$ solution with three kinds inhibitors within 1 to 12 days. The inhibitors are an amino-alcohol (AMA) reagent, a commercial MCI inhibitor and a synthetic ternary amine-carboxylates based inhibitor. In the beginning, the solutions did not add any chloride but 3% the inhibitors. As expected, the polarization resistance values of the steel immersed in CH solutions with different inhibitors increase enormously from 1 day to 12 days, particularly the ternary amine-carboxylates based inhibitor showed the best performance in the whole process, the highest LPR value reach to $1\times10^3$ kohms.cm$^2$. The commercial MCI inhibitor gives the middle value and the AMA lowest. The results showed that the ternary amine-carboxylates inhibitor was more efficient when it was used in the solution of chloride absence, and the stabilization effect on the passive layer of the inhibitor was pronounced in a relatively long process. However, when NaCl (10g/l) was added after 12 days immersion of electrodes in the solution containing inhibitors, the LRP of the steel were measured two days or four days later, as seen in Fig.3, although the ternary amine-carboxylates inhibitor gives a relatively higher residual values, while the AMA and the commercial MCI inhibitor receive a very low residual LRP values. That means the inhibition effect was decreased. The inhibition effect of the inhibitors was also investigated by the use of electrochemical impedance spectroscopy (EIS). Fig.4 depicts the Nyquist plot obtained on two steel electrodes immersed in solution containing 4g/l of inhibitor with or without NaCl addition and the control sample is in CH solution contaminated with 4g/l NaCl only. It can be seen that the addition of an monoamine-carboxylate based inhibitor to the CH solution without chlorides have the highest impedance, but the addition of the same inhibitor to the
solution contaminated with 4g/l NaCl resulted in a big drop in the value of the general impedance, although there is an increment in the value of the impedance than that of in the solution contaminated with 4g/l NaCl only. The phenomenon indicates that the chloride-resistant capability of AMA and the commercial MCI as well as the monoamine-carboxylate inhibitor in the aggressive solution is not so good. The reason may be because the deficient protective layer can not resist to the aggressive action of chloride ions or the chloride ions interfere with the formation of the passive film on the steel surface [4,7-9]. That means the AMA and amine-carboxylate maybe only suit for the use of preventive admixtures in concrete ahead of chloride ingress.

3.2 The curative effect of inhibitors addition
For the old concrete structure contaminated with chloride salt, painting the curative MCI on the concrete surface is recommended to rehabilitate the corroded reinforcing steel in concrete. To develop a curative inhibitor and test the self-repairing effect, the steel was kept
in the CH solution containing 1% NaCl (without inhibitor) until the steel corrosion initiation. After 12 hours the corrosion potential and LRP was measured and the calculated corrosion current showed the corrosion activity was noticed and then 4.38% (43.8g/l) curative inhibitor (named BT1000) was added. As depicted in Fig5, before addition of the inhibitor, the corrosion current was 4.02 µA/cm², after the inhibitor addition the corrosion current starts to decrease and 24 hours later it reaches 0.20µA/cm², about one twentieth of the initial ones. After 96 hours it reaches 0.092 µA/cm², which is about 0.25% of the initial ones. This behaviour clearly shows that this inhibitor is able to decrease remarkably the corrosion rate of the steel even when it is initially under localised corrosion attack. For further testing the curative effect of the inhibitors, the electrochemical behaviour of the steel was also studied by potentiodynamic scanning. Fig.6 depicts the potentiodynamic polarisation curves obtained in the Ca(OH)₂ solution contaminated with and without inhibitor addition. The control sample was kept in the initial aggressive solution (1% NaCl, no inhibitor) for 36 or 60 hours, the open circuit potential Ecorr shifted to a more negative value, allowing developing stronger corrosion activity. Then the anodic polarisation curves and the break potential Ebreak (about +100mV) was measured. Another steel sample was kept in the same aggressive solution (1% NaCl) but with 3% inhibitor for 36 hours. Then the breakdown potential Ebreak (about +500mV) was also recorded during the anodic polarisation process, as seen in Fig.6 (in symbol □), the results show that in the solution containing 3% curative inhibitor the corrosion activity was strongly reduced and the Ebreak was enhanced effectively. Fig.6 (in read symbol ●) depicts the second anodic polarisation curves of the breakdown steel sample in the same solution with both chlorides and the curative inhibitor after 24 hours. The results show clearly the steel electrode which was broken down through the first strong polarisation has been rehabilitated and the polarisation current was strongly reduced during the past 24 hours. The break potential Ebreak was also improved from first time about +500mV to more than +600mV. The same behaviour was observed once more after another 36 h of dipping in the solution with both chlorides and the curative inhibitor, as seen in Fig. 6 (in blue ▲). The results suggest that the inhibitor has an effective self-healing ability of the defects and allow the re-formation of a stable protective film on the steel electrode, which protect the steel surface from destruction even when the corrosive chloride ion presence in the solution. The most probable mechanism may be based on the “hard/soft acid/base” rule. Some corrosion activity spots induced in the process of anodic polarisation make the pure iron exposed to the inhibitors in the solution and the “soft base” groups of the inhibitor may be adsorbed better on the “soft acid” of pure iron in the active than in the passive state. At the same time the activity spots create more anchorage points and the inhibitor start to block the active sites and cover the entire steel surface again, leading to a decrease of the corrosion current of the system. Further more the inhibitor layer seems to have the capacity to bind chlorides through the protonated amino groups of the inhibitor. The consequence is thus an increase of the threshold chloride content for corrosion initiation on the steel surface [8]. Moreover the strong curative capability of the inhibitor may be related to the formation of self-assembled monolayers. However, further investigations are necessary to prove the curative mechanism provided by XPS and electrochemical scanning tunnelling microscope (ECSTM) results.
3.3 The integrative effect with surfactant addition

For fast migrating of inhibitors in concrete and further improving long-term stability of protective film on the steel, some surfactants should be added in the inhibitors. To sieve surfactants and test the integrative effect of the curative inhibitor with surfactant, the testing inhibitors are varied into two kinds named BT1000J and BT1000E according to the mixed surfactant. For comparison with other inhibitors, two commercial inhibitors are also tested. Figs.7-10 reports the Nyquist plot and Bode-phase diagram obtained in 1-3% NaCl CH solution with or without the inhibitors addition.
Analysis of the experimental data was done by fitting the results to an equivalent circuit. A model with the circuit form $R_{\text{sol}} (Q R_t)$ was considered to fit the data. The experimental response was fitted so as to receive the data in Table 1, where: $R_{\text{sol}}$ and $R_t$ represent the solution resistance and the charge transfer resistance; $Q$ represents equivalent element $n$ is index of reflecting the homogeneity of the solid/liquid interface; $n$ equals one means that $Q$ represents the double layer capacitance; $n$ equals zero means $Q$ is a pure resistance; $n>0.6$ the $Q$ behaves approach to capacitance [10]. As seen in Fig.7-8 and Table 1, the addition of the inhibitors BT1000J and BT1000E to the solution contained 1% and 3% NaCl resulted in a greater increment in the value of the impedance than that of the control ones label C1 and C3. The fitting results of the label E1 and E3 show that the protective film becomes more insulating, which the date of $R_t$ is more than $2.0\times10^6$ ohm.cm$^2$, while the date of $Q$ about $8.0\times10^{-7}$ F/cm$^2$, approaching the behaviour characteristic of a capacitor. The results in this work clearly show that the inhibitors with surfactant behave excellent inhibiting properties. Figs.9 and 10 suggest the presence of two time constants in the spectra. The time constant observed at higher frequencies probably describes the behavior of the film formed on the surface, while the time constant at lower frequencies is associated with the electron transfer reactions occurring in pores and defects of the film formed on the surface [8]. The remarkable increase of the phase angle in the high frequency region of the spectra with 1-3% BT1000E inhibitors in CH solution contained 1% and 3% NaCl, which reaches values around 85°, suggests that a compact and homogeneous protective film is present on the surface, strongly hindering the corrosion processes. And the increase of the phase angle in the low frequency region of the spectra with BT1000E inhibitors also suggests the less electron transfer reactions occurring in the film formed on the surface than that of control samples (label C1 and C3). This is completely in agreement with the strong increase of LRP values and notable decrease of the current value in Table 2. That further proves that the presence of inhibitors causes a strong reduction of the anodic activity and helps to the formation of a protective layer on the surface that complex the chlorides ions.
4. SUMMARIZATION AND CONCLUSION

This study was performed to test the inhibition abilities of an amino-alcohol and amine-carboxylates based corrosion inhibitors in the solution of simulating chloride contaminated concrete pore water. The result shows that the amino-alcohol and the amine-carboxylates was efficient in the CH solution of chloride absence and only the ternary amine-carboxylates showed an acceptable inhibitive action in simulating chloride-contaminated concrete pore solution. This suggests the AMA and the amine-carboxylates may be only suitable for the preventive use mode in concrete ahead of chloride ingress. The tests also show that the curative inhibitor is able to remarkably decrease the corrosion rate of the steel in the chloride
condition even when the steel was broken down by the strong anodic polarization. The test of integrative effect with surfactant addition in the inhibitor further indicate that the charge transfer resistance and the linear polarization resistance have a great increase in the presence of the curative inhibitors. The Nyquist plot and Bode-phase diagram suggests that the protective layer at the surface of steel becomes homogeneous and compact in the 1-3% NaCl CH solution with curative inhibitor addition. The results creates an opportunity to develop a active corrosion protective admixture with self-repairing ability to control the corrosion of steel and rehabilitate the old reinforced concrete structures in chloride condition.

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