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Effectiveness of Corrosion Inhibitors in Simulated Concrete Pore Solution

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ABSTRACT

Steel embedded in concrete is normally in a passive state against corrosion due to a thin iron oxide layer that forms on the steel surface and remains stable in the high alkaline environment of the concrete. This protective film must be destroyed (depasivation) and this can be mainly done in two ways: by the attack of chlorides on the steel (seawater, de-icing salt, unwashed sea sand, admixtures etc.) or by carbonation. Corrosion inhibitors may be a good alternative to protection steel against corrosion due to its lower cost and easy application. Many researchers are inclined to use surface applied corrosion inhibitors and prefer to use the Cl^- /inhibitor parameter as an indication of chloride inhibitor threshold level. The objective of this study was to fill the gap left by public research in developing methods of corrosion control of reinforcement in concrete by synthetic solutions to emulate concrete environment. Three inhibitors were distinguished as passivation inhibitors in real solution extract and synthetic. In this study the tests with calcium nitrite (CNI), sodium monofluorophosphate (MFP) and ethanolamine based inhibitors showed reductions in the overall rates of corrosion after the inhibitive treatments.

Keywords:

Concrete, Corrosion, Chloride, Carbon Steel, CNI, AMA and MFP.

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1. Introduction

Minimising the direct and indirect costs of marine structure maintenance and maximising the available capacity is critical to the economic competitiveness of an expanding European Union. The use of corrosion inhibitors – a developing technology - as part of a repair strategy may provide a cost effective solution. A bibliography of over 180 references was assembled. A detailed review was made of material published in the last fifteen years. The review embraced some aspects of CNI, AMA and MFP based inhibitors, used in new construction and repair methods based on cementitious mortars but the main focus was on surface applied corrosion inhibitors. Several studies have been conducted to assess the effects of chloride ions in simulated pore solution. A summary of available literature was given to the most commonly used inhibitors such as CNI, AMA and MFP in artificial concrete pore solutions. In tests with calcium nitrite, sodium monofluorophosphate and ethanolamine based inhibitive treatments Monticelli et al (2000) [1] observed moderate reductions in the overall rates of corrosion after the inhibitive treatments. To ensure this effectiveness the ratio between

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inhibitors and chloride ions has to be relatively high (approximately 1) (Elsener et. al. 1999) [2]. Mammoliti et al (1999) [3] have shown that calcium nitrite addition into simulated pore solution at a level of 0.1% was able to repassivate pre-corroded steel in 1% chloride. When the chloride was added to the simulated pore solution already containing 0.1% calcium nitrite, the increase in chloride up to 1.5–2.0% did not change the potential or the corrosion rate significantly [Ngala, et al, 2002] [4]. However, CNI in solutions of very high pH value the concentration of Ca^{2+} ions is strongly limited by the solubility product of $\text{Ca}(\text{OH})_2$. The presence of CNI in the pore solution leads to precipitate calcium hydroxide (and consequent reduction in pH) [Li et al, 2000] [5]. Kawamura et al (1997) [6] measured the $[\text{Cl}^-]/[\text{NO}_2^-]$ ratio both in pore solution and in mortar specimens. The free chloride concentration in the pore solution decreased and the OH^- content increased with the time of aging. The $[\text{Cl}^-]/[\text{NO}_2^-]$ ratio remained fairly constant and achieved a value of about 0.8 for 0.5% of admixed NaCl and 1% of sodium or calcium nitrite. The best inhibiting capacity was noted when the inhibitor was introduced in the solution before the contamination with chlorides, what gave a reduced effect especially when chlorides were present in the simulated pore solution [Benzina et al, 2008] [7]. In salt solution the AMA-based inhibitor delayed the initiation of corrosion and reduced the I_{corr} (when the NaCl concentration is 0.3%, I_{corr} was 0.45 and $0.1\mu\text{A}/\text{cm}^2$ for the control and the inhibitor samples, respectively) [Heiyantuduwa et al, 2003] [8]. AMA inhibitors are best used to extend (or help to achieve) the required service life by deferring the initial time to depassivation, and/or through reducing the rate of corrosion once corrosion is propagated, or retard incipient action (ring anode) [9]. Passivation due to the amino inhibitor is reached by the formation of an adsorbed layer on the steel surface. When the critical concentration ratio is not reached, the layer is partly destroyed, and the corrosion damage is rather localized. When the stabilization of the passive state is reached due to the inhibitor and subsequently the

concentration of the inhibitor is reduced, the initiation of corrosion might reoccur (the ratio of concentrations inhibitor/ Cl^- is critical also in such cases) [10]. The sooner the inhibitor is introduced after corrosion propagation the more effective it is [11]. The long-term concentration of the inhibitor near the reinforcement, which may decrease over time due to leaching and evaporation, is a crucial parameter for the effectiveness of the inhibitor as part of a repair strategy [12]. Monofluorophosphate seems slightly efficient in simulated pore solution and in mortar and higher MFP concentration being slightly better (0.05, 0.1 and 0.5 M MFP and 0.5 M NaCl) [Alonso, 1996] [13]. The effectiveness of MFP increases with the inhibitor concentration in alkaline solution [Hope and Thompson, 1995] [14] and the minimum efficient ratio MFP/ Cl^- (0.5 M NaCl and 0.5 M MFP) is reported to be 1–1.5 [Lafave et al, 2002, Palmer and Malic, 2000] [15,16]. The aim of this work is study of the basic mechanism of inhibitors for corrosion control of reinforcement in concrete by tests in simulated concrete pore solution.

2. Experimental program

This part consists of two methods based on influence of (CNI, AMA and MFP) inhibitors firstly, in simulated concrete pore solution and secondly, influence of AMA in extracted cement solution because AMA is claimed to inhibit corrosion by penetrating concrete and adsorbing on the metal surface more than CNI and MFP. The demonstrate AMA in extracted cement solution is new applied to evaluate the influence of inhibitors in blended cement extract solution. The laboratory tests in simulated concrete pore solution included exposure of steel specimens in pore solution with analysis of corrosion damage and passive layers; exposure of steel specimens in pore solution with chloride and analysis of corrosion damage; determination of potentiodynamic polarization curves in simulated pore solution; determination of electrochemical impedance spectra in simulated pore solution.

2.1 Materials and methods

In order to achieve the goals of this study several laboratory tests in simulated concrete pore solution were performed. These were as follows:

- Exposure of steel specimens in solution with analysis of corrosion damage and passive layers,
- Exposure of steel specimens in artificial pore solutions with Cl^- and analysis of corrosion damage,
- Determination of open circuit potential E_{OC} , potentiodynamic polarization curves in simulated pore solution,
- Determination of electrochemical impedance spectra in simulated pore solution,
- Influence of AMA inhibitors in blended cement extract solution

Corrosion inhibitors, CNI, AMA and MFP were added to the different solutions separately. The dosage of CNI is 300 ml/l and the dosage of AMA is 4% (v/v) which is equivalent to (40 ml/l). In this work the dosage of MFP is 2% equivalent to (20g/l) and which is below the recommended amount (5%) to check the inhibition effect in the corrosion process. Experiments were conducted using carbon steel bars, and with a diameter of 8 mm), reference steel. The inhibited steel surface was approximated as a cylinder with a height of 2 cm corresponding to a surface area of 5.02 cm^2 . Each sample was allowed a period of 24 hours to stabilize in the solution before applying the test. Firstly, a saturated calcium hydroxide solution (noted S1) has been used to simulate the aqueous alkaline content of the (non-carbonated) concrete pore solution, with an approximate pH of 13. Secondly to simulate the aqueous phase of a concrete contaminated with chloride, was used to obtain an electrolyte designated by S2 (see Table 1). This contains $\text{Ca}(\text{OH})_2$ saturated solution and NaCl . This chloride content is higher than critical threshold by approximately 20 times, because most of the existing research generally agrees that the Cl^-/OH^- threshold ratio for

carbon steel is < 1 . The initial pH measured was 13, but, it dropped to a value of 12.5 ± 0.05 due to the chloride addition and possible carbonation from air during poring into the corrosion cells (Nedal, 2009) [17]. The range was 3.5% for chloride concentration. In some experiments the inhibitor was added to the simulated pore solution (S1) at the very beginning, when the steel surface was still clean, to investigate delay of time to depassivation. In other experiments the inhibitor was added the simulated pore solution (S2) after the corrosion already started to investigate the influence on corrosion rate control. The results of the measurements obtained in simulated pore solution represent the basis for further investigations in concrete.

2.2 *Extracted cement solution*

This part is concentrated on the influence of AMA in extracted cement solution. Pore solution extract for a concrete mix of water to cement ratio of 0.4 is (Hydroxyl OH^- , 700 mmol, Sodium Na^+ , 192 mmol, Potassium K^+ , 592 mmol, Sulphate SO_4^{2-} , 44 mmol, Calcium Ca^{+2} , 2 mmol). The pH found in extracted cement solution is 13.7. The use of AMA in extracted cement solution is new applied in our laboratory. The inhibition efficiency of the AMA to the surface of six steel (repeatability for one test) placed in extract solutions more or less corrosive and simulating more or less degraded concrete was investigated through electrochemical methods Figures (1). Free corrosion potential measuring E_{OC} , Cyclic polarization test and potentiodynamic scan (GC) were applied after 1 day and 2 days up to 8 days of immersion. Experiments were conducted using carbon steel bars, and with a diameter of 8 mm), reference steel.

2.3 *Electrochemical Measurements*

In order to apply the open circuit potential (E_{oc}) of a metal, the potentiodynamic scan or the cyclic polarization scan, three electrodes are immersed in the testing solution and connected

to a Biologic Ec- Lab potentiostat a device that is used to apply on over potential and record the induced current. Potentiodynamic scan and cyclic polarization are similar to the Cyclic polarization test. These tests were applied after 1 day and 2days up to 8 days of immersion. The data obtained for each time from six steel (repeatability for one test). The electrochemical impedance is then automatically calculated from this data in lab measurements. The experiment is controlled by data logging system and analysis is done using software provided by the manufacturer.

2.3.1 Open Circuit Potential Measurements EOC

The free corrosion potential is a good indication of the metal's tendency to corrode in a certain solution. Having a relatively fixed (not drifting) potential is an indication that the sample has stabilized in the solution. The test parameters are:

- The total time: this is the test duration in seconds. The sample's potential was measured against the Saturated Calomel Electrode (SCE) for duration of 60 seconds.
- The sample period: this parameter determines the spacing between data points in seconds. The sample period was 1 second.
- The stability: that is used to tell the system the definition of a stable potential. When measuring the open circuit potential, if the drifting rate falls below the stability this will result in terminating the experiment immediately. This parameter has units of mV/sec. The stability was set to be zero mV/sec. This means that the test will be terminated only when the total time ends.
- Sample Area: the sample surface area in (cm²) that is immersed in the solution.

2.3.2 . Potentiodynamic Scans

The potentiodynamic scan was used to measure corrosion current density, and then corrosion rate was calculated. For every sample, the potentiodynamic scan was applied to determine the corrosion current density i_{corr} at that time. The test parameters are:

•Initial E: is the starting point for the potential sweep in Volts. The initial potential E was -100 mV vs. E_{OC} .

•Final E: is the ending point for the potential sweep in Volts. The final potential E was 1000 mV vs. E_{OC} . This scan range (E_{OC} from -100 to + 1000 mV) enabled the estimation of i_{corr} without destroying the sample. Testing further anodic potentials would force the sample to corrode (i.e., destructive testing).

•The sample period: the sample period was 1 second.

•Scan Rate: is the speed of the potential sweep during data acquisition. Its unit is mV/sec. Very high scan rates lead to unreliable data; however, very low scan rate elongate the test period. The applied scan rate was 0.1 mV/sec.

•Density: is the density of the metal tested in g/cm^3 . This parameter is used for corrosion rate calculation.

•Equivalent Weight: is the theoretical mass of metal that will be lost from the sample after one Faraday of anodic charge has been passed. This parameter is used in corrosion rate calculations.

•Initial Delay: this option is used to allow the open circuit potential of the sample to stabilize prior to the potential scan. The delay time is the time that the sample will be held at its open circuit potential E_{OC} prior to the scan. The delay may stop prior to the delay time if the stability criterion for E_{OC} is met. The delay time parameter is active only if the initial delay is turned on. This option was turned off in all the experiments.

•Extrapolation of the corrosion current density i_{corr} was made with the help of potentiostat Analyst software.

2.3.3 Cyclic polarization

Each sample was allowed a period of 24 hours to stabilize in the solution before applying the test. The test parameters are:

•Initial E: is the starting point for potential sweep; initial E was -0.025 V vs. E_{OC} .

•Final E: is the ending point for potential sweep; final E was +0.025 V. The forward scan rate was 0.5 mV/sec. The test is used mainly to investigate the metal's tendency to pitting corrosion in a certain environment and this ratio may be reach to -600 mV to +600 mV according to aggressive environment.

•Apex E: is the end potential for the anodic (upward) scan. Apex E (E_{rev}) is one of two conditions that will terminate the forward sweep and initiate the reversal scan if it is reached and the Apex I is not exceeded yet. Apex E was one V vs. E_{OC} .

•Apex I: is the corrosion current density that is indicative of pitting initiation and it is one of two conditions that will terminate the forward sweep and initiate the reversal scan if it is exceeded by the absolute current of the sample. The Apex I was $1 \mu A/cm^2$.

2.3.4 Electrochemical Impedance Spectroscopy (EIS):

Literature on the applications of EIS shows that it has great advantages over other techniques in studying the passive film formation providing the use of low frequencies of AC signal [Pruckner, 2001] [18]. The test parameters are:

Initial Frequency: is the starting point for the frequency sweep during the data acquisition phase. The frequency unit is Hertz. The initial frequency was 100 kHz.

Final Frequency: is the ending point for the frequency sweep during the data acquisition phase. The final frequency was 100 mHz for cathodic electrochemical treatment and 50 mHz for inhibitor treatment. Testing lower frequencies would make the test duration too long.

Points/decade: is the number of data points in each decade frequency. The value used was the default value of 70 -90 points per decade.

AC Voltage: is the amplitude of the applied AC (alternated current) signal to the working electrode. The unit is in root mean square (rms) mV. The excitation AC signal should be small in order to keep in the linear region (i.e., the AC current response will be in the same

frequency but with phase shift) and not to destroy the sample. The applied AC voltage was 10 mV rms.

DC Voltage: is the applied DC (direct current) voltage on the working electrode. The purpose of the experiment was to study the properties of the passive film that is formed naturally on the metal surface. Thus, samples were held at their free corrosion potential EOC (i.e., DC Voltage = 0.0 vs. EOC).

Estimated Z: is a rough estimate of the cell's impedance at the Initial Frequency entered. This value is used to minimize the number of trials that the system operates to calculate the cell's impedance at the first data point. After the first point, this value is not important as the system uses the last estimated value for Z to calculate the new Impedance with the new frequency.

Figure 2a shows a schematic of the equivalent circuit R(QR) for non treated steel used in EIS data fitting. The proposed electric equivalent circuit $R_{el} + C_f/R_f + C_{dl}/R_{ct}$ for steel treated with inhibitors by [Nedal, 2009 and Pruckner 2001 [17, 18] in their work to study passive film formation on carbon steel in alkaline solutions is given in Figure 2b. This circuit consists of the solution ohmic resistance R_{el} connected in series to two loops. The first loop represents the double layer capacitance C_{dl} and the charge transfer resistance R_{ct} . The other loop represents the passive film formed on steel surface in the high alkaline solutions where C_f and R_f are the faradic capacitance and the ohmic resistance of the film, respectively. It is believed that this circuit introduces a reasonable explanation of the ongoing electrochemical process on the metal surface immersed in a high alkaline solution.

Since the capacitance (c) equals the charge built up in the capacitor (q) divided by the potential (V) (the free corrosion potential in this case), a metal in a passive state (i.e. less metal dissolution-less charge transfer between the metal surface and the electrolyte) will have less capacitance than an actively corroding metal. In other words, for a constant exposed area

258 an active corrosion process will lead to an increase in the total charge transfer, which leads to
 259 increased film capacitance [Nedal, 2009,Sahoo and Balasubramaniam 2008] [17, 19].

260 This electrochemical impedance of the system presented in the following equations.

261 The impedance Z of a resistor equals:

262 $Z = R$ [5.1]

263 Where R is the resistance in ohms.The impedance of a capacitor equals:

264 $Z = \frac{1}{j\omega C}$ [5.2]

265 Where C is the capacitance in farads, j is $\sqrt{-1}$ and ω is the angular frequency $\omega = 2\pi f$.

266 The total impedance of a system Z_{total} when the components are connected in series equals:

267 $Z_{total} = Z_1 + Z_2$ [5.3]

268 The total impedance of a system Z_{total} when the components are connected in parallel equals:

269 $Z_{total} = \frac{Z_1 Z_2}{Z_1 + Z_2}$ [5.4]

270 Thus, the total impedance equals:

271 $Z_{total} = R_{el} + \frac{R_f}{1 + R_f(j\omega C_f)} + \frac{R_{ct}}{1 + R_{ct}(j\omega C_{dl})}$ [5.5]

272 Where

273 R_{el} : resistance of electrolyte

274 R_f : film resistance formed in alkaline solution

275 R_{ct} : charge transference resistance

276 The other loop represents the passive film formed on steel surface in the high alkaline
 277 solutions where C_f and R_f are the faradic capacitance and the ohmic resistance of the film,
 278 respectively.

279 A capacity film reduction (C_f) that leads to a film thickness increase (equation (5.6))

280 expressed as $C_f = \epsilon_o \epsilon_r A/d$ [5.6]

Where ϵ_0 is the vacuum permittivity (8.85×10^{-14} F cm⁻¹), ϵ_r is the dielectric constant (≈ 1), A the active surface and d the thickness of film.

2.4 SEM and EDS analysis.

To characterize the influence of coating in protection of steel from corrosion, SEM reveals the morphology and composition of film on the surface of steel created by inhibitive treatments in simulated concrete pore solution. The overall analysis SEM and EDS has identified the elements on surface of steel treated by inhibitors.

3. Results and discussion

3.1 Results of Carbon Steel Immersed in Synthetic Solutions Emulating Concrete Admixed with Inhibitors Open circuit potential.

3.1.1 Open circuit potential

Fig. 3 shows the open circuit potential (also referred to the rest potentials) test obtained from linear polarizaton tests for carbon steel samples immersed in synthetic concrete pore solutions S1 as after 1 hour, untel 8 days of immersion. Each point in this figure is the average of six points. At the first hours of the addition of inhibitors the rest potentials E_{OC} are respectively around -100 mV for the CNI, -460 for MFP in comparison with S1 without inhibitors and -330 mV for AMA. Guidance for interpretation of results is given in the ASTM standard C876-99[20] and is summarized in Table 2. The systems showing potentials lesser negative than -276 mV versus SCE are treated as passive systems and systems showing more negative than -276 mV versus SCE are treated as active. Thus, the rebars in S1+ CNI are probably passive whereas an active corrosion probably takes place on the rebars in S1 without inhibitor and with MFP. The rest potentials increase with time. Eight days after addition of inhibitors, the rest potentials E_{OC} of S1+CNI are respectively between -50 and -20 mV and between -220 and -330 mV for all inhibitors added in S1. These results indicate adsorption of an inhibitor film on the iron surface which leads to a slowdown of the corrosion probability after

the inhibitor addition. The potential of steel without inhibitors increases due to the presence of passive layer of oxides (Fe_3O_4 and Fe_2O_3) on the surface of steel.

3.1.2 Corrosion current evolution

The corrosion currents obtained from applying cyclic polarization curves for S1+CNI, S1+AMA and S1+MFP are illustrated in Figure 4. According to RILEM studies [Andrade et al. 2004] [21], 4 ranges of corrosion activity can be distinguished from negligible, to weak, to moderate and up to high Table.3. Each point of the corrosion current in this figure is the average of six points. After addition of inhibitor, the data shows lower corrosion currents with time and after 8 days the corrosion current range is from 0.12 to 0.46 $\mu\text{A}/\text{cm}^2$ for S1+CNI, S1+AMA respectively. For rebar S1+MFP, corrosion activity after 8 days is (3.5 $\mu\text{A}/\text{cm}^2$). In cases, S1+CNI, S1+AMA, the corrosion activity is constant with time. For S1 without inhibitor and MFP the current also is almost constant and more than 1 $\mu\text{A}/\text{cm}^2$ corresponding to high rate corrosion. So the corrosion process is probably slowed down but not stopped with S1+MFP. The order of I_{corr} from high to weak is: S1 = S1+MFP, S1+AMA > S1+CNI.

3.1.3 EIS measurements in pore solution

The electrical parameters ($C_{\text{dl}}, R_{\text{ct}}$) obtained through fitting EIS data, using the electric equivalent circuit R(QR) and $R_{\text{ct}} + C_{\text{f}}/(R_{\text{f}} + C_{\text{dl}}/R_{\text{ct}})$, are listed in (Table 4). The values of E_{pit} in table 4 illustrate that inhibitors increase the pitting resistance of the metal. EC-Lab software was used in data fitting. The mathematical method used was Levenberg- Marquardt method. Figure 5 shows a Nyquist plot of the impedance of carbon steel immersed in fresh concrete pore solution with various amounts of inhibitors added to the solution in a period of 8 days. It can be noticed that the low frequency portion of the impedance spectra (on the right hand side) increases with presence of inhibitor in the solution as a sign of passivity does not break down. Figure 5 shows the main conclusions for all types of inhibitors, the order of inhibition is: S1+AMA > S1+CNI > S1+MFP > S1 according to the values of R_{ct} .

In the Nyquist impedance two time constants (one at high frequency HF and another at low frequency LF) for treated steel, and thus the capacitive loop observed in the Nyquist plots is consisted of two non-decoupled capacitive loops just for CNI. For the carbon steel film, the double layer capacitance $C_{dl} < 2.5 \mu\text{F}/\text{cm}^2$ shows that a small part R_{ct} of the inhibited steel surface is involved in the electrochemical reactions at the steel/solution interface [Simescu and Idrissi, 2009] [22]. The corrosion reaction occurs only on a very small fraction of the total inhibitor steel area.

Basically, the passive film has a high resistivity with inhibitors; however, it decreased with reference specimens in the solution S1. The inhibitor layer of iron oxides/hydroxides surface film seems to cover the entire surface blocking the active sites and the total impedance of the system increases continuously. Thus, the increase in the sum of the charge transfer resistance and the film resistance ($R_{ct} + R_f$) was observed in Table 4. The faradic capacitance of the passive film C_f decreased with inhibitors addition to the solution due to the decrease of charge transfer at the metal/electrolyte interface and reduction of capacity film (C_f) that leads to a film thickness increase. It is remarkable that the film capacitance MFP decreased by about six times than AMA and by three times than CNI. R_f and C_f are absent in diagrams corresponding to reference specimens immersed in alkaline solution, during only 8 days, due to the 8 days is not enough formation film on the surface of steel and also absence of inhibitors.

3.1.4 Cyclic polarization curve

It can be noticed that the metal had a passive region (decreased applied over potential and current density) that started immediately after the Tafel area ($E_{OC} \pm 50 \text{ mV}$) for CNI and between -220 and -400 mV for all inhibitors added in S1 and continued until E_{pit} was reached Figure 6. The results of E_{pit} are shown in Table 4. In these solutions, the hysteresis loop was determined but E_{rev} seems adherent because corrosion inhibitors are not used to totally stop corrosion and E_{pit} , which is an indication that the metal is repassivate and able to resist pitting

corrosion at these inhibitors types. In addition, the recorded i_{corr} of MFP in reverse scan is higher than other inhibitors. Perhaps a longer exposure time in that solution with MFP was needed to increase the pitting resistance of the metal.

3.1.5 Surface analysis with SEM

a). SEM of carbon steel in S1+MFP

Figure 7b shows the SEM on the surface of the samples immersed during 1 week in solutions S1 with MFP inhibitor. The inhibiting action of sodium phosphate showed that phosphate compounds form a protective layer on the steel surface when immersed in alkaline solution without chlorides. A passive layer of Fe_3O_4 , $\gamma\text{-Fe}_2\text{O}_3$ and $\text{FePO}_4 \cdot \text{H}_2\text{O}$ results of hydrolysis $\text{Na}_2\text{PO}_3\text{F}$ in aqueous and neutral media to form orthophosphate and fluoride [Alonso et al, 1996] [13]. But phosphate compounds characterized by spherical glassy plate of sand rose, lamellar shapes crystal exists on the surface of steel.

b). SEM of carbon steel in S1+AMA

The surface of the samples immersed during 1 week in solutions with inhibitor is depicted in Figure 7c. The one zoom images shows the presence of an oxide film due to displacement of the first hydrated monolayers of the iron oxide film. Smialowska et al (1981) [23] on the other hand, showed that the passive films formed in alkaline solutions are closer to an iron oxyhydroxide (FeOOH) than to $\gamma\text{-Fe}_3\text{O}_4$ or Fe_2O_3 Smialowska et al (1985) [24]. The uniform film deposited over the surface and practically there are no signs of corrosion. The film becomes much thicker, more uniform and amino compounds are present on its surface. This behaviour is according to the literature, which suggests that the organic inhibitors usually adsorb on the surface leading to the formation of a thin adsorbed layer [Jamil et al. 2003] [25]. The SEM observations show that the (N-CH bonds) is compact well crystallized and covers completely the steel surface. The film observed in big area characterized by eggs shape or cotton-balls shaped due to its big thickness. These positive charged groups are likely to form

at the expense of inhibitor interaction with water molecules (from hydrated layers compounds) on the iron surface [Jamil et al, 2003] [25]..

c). SEM of carbon steel in S1+CNI

The results of influence of CNI on microstructure are shown in Figure 7d. A stable passive layer of γ -FeOOH is formed on the surface of steel. This film is insoluble in aqueous alkaline solution and creates a solid layer on steel surface blocking the transport of ferrous ions into the electrolyte. As can be seen from Figure 7d mixture of flower-like pattern of α -FeOOH (goethite) and γ -FeOOH (lepidocrocite) and plate-shaped of calcium hydroxide are presented [Soylyev and Richardson, 2008] [26]. The inner layer composed mainly of magnetite is compact, dense and adherent.

Results of Carbon Steel Immersed in Synthetic Solutions Emulating Concrete Admixed with Inhibitors Open circuit potential

3.2 Results of Carbon Steel Immersed in Synthetic Solutions Emulating Concrete Admixed with Inhibitors under Chloride Ion Attack.

3.2.1 Open circuit potential

Figure 8 shows the open circuit potential in case of pore solution admixed with inhibitors under amount of chlorides 35 g/l. The rest potential value for S2 decreases significantly after 8 days (due to the presence of chloride). A drop in the corrosion potential was happened by other researchers as an indication of reaching the critical chloride limit [Hausmann, 1967 and Li and Sagues, 2001] [27,28]. For S2+MFP and S2+AMA the rest potential has approximately the same value and increases with time. This result due to two reasons: the first reason is the competition between chloride and the film of inhibitor which leads to increase resistivity of the film. the second reason is that protonated amino group's bind chloride so the concentration of chloride required for initiation of corrosion. This is an important feature when the inhibitor is used in concrete structures, since it may help to increase the Cl^-/OH^- threshold ratio, which is one of the more important parameters in controlling the corrosion in

reinforced concrete structures [Jamil et al, 2003] [25]. AMA is recommended as complementary technique for reduction in time of regeneration of the passivity is obtained. CNI is not affected by presence of chloride see Figure 8

3.2.2 Corrosion current evolution

Figure 9 shows the corrosion current density (i_{corr}) obtained from carbon steel samples immersed in S2. With time, the corrosion currents for S2+CNI remain low and closed to values obtained with no chloride. The previous result indicates that calcium nitrite not affected by the presence of chloride and this due to that nitrite does not incorporate into the passive film, but reacts with the anodic corrosion products in the early stage competing with the chloride ions and hydroxide ions. It helps to repair the flaws, which are caused by chloride dissolution of the oxide film to the soluble chloro complexes of iron [El-Jazairi and Berke, 1992 and Berke and Weil, 1994] [29,30]. But S2+AMA and S2+MFP show corrosion current which is decreasing with time and ranging from 2.5 to 7.5 $\mu\text{A}/\text{cm}^2$ at 8 days, indicating a lower corrosion activity of the rebars. Each sample needs enough time to whether develop its passivation layer or actively corrode. For S2, the corrosion currents of rebars increase significantly with time because of the corrosion products.

3.2.3 EIS measurements in pore solution (Initiation of corrosion (prevention of corrosion))

In this group of experiments the inhibitor was firstly added to the pure simulated pore solution, and afterward chlorides were successively added. The main goal of these experiments was to investigate whether the inhibitor additionally stabilizes the passive state of clean, already passivated steel surface. At the beginning, it can be seen in Figure 10 that the inhibitor increased the total electro-chemical impedance of the system, as well as changed the profile of the spectra. The significant reduction of the total impedance was observed when the

chloride concentration in pore solution reached a rather high value. From the measured spectra presented as Nyquist plots it can be seen that the inhibitor considerably changed the shape of the spectrum. It can be therefore concluded that the structure of the passive layer due to the inhibitor differs from the layer in pure pore solution. The electrical parameters are listed in (Table 5) at 8 days. EIS data for S2 containing CNI, AMA and MFP aged 8 days in the same aggressive solution. Calcium nitrite is an anodic inhibitor. It functions by oxidizing corrosion product - ferrous ions - to ferric ions that precipitate in the alkaline solution of the concrete and form a protective layer on the reinforcement. The precipitate functions as a film repair because the ferric ions are insoluble in aqueous alkaline solutions and block the transfer of ferrous ions into the electrolyte. This is data due to competition between the formation and local destruction of the film obtained by the slow inhibitor dissolution. This classical corrosion mechanism leads to the diminution of R_{ct} and to the increase of the double layer capacitance C_{dl} while R_f increases in comparison with S1. This evolution corresponds to the electrolyte diffusion into the film pores. The order of inhibition is: $S2+CNI > S2+AMA > S2+MFP > S2$ according to the values of R_{ct} .

3.2.4 . Cyclic polarization curve

Figure 11 represent the potentiodynamic polarization curves of steel in S2 solution without and with CNI, AMA and MFP. A higher significant potential shift is observed between S2 with inhibitor and the S2 without inhibitor. It can be noticed that the pitting potential for CNI equal to +200 mV vs. SCE and this help the metal to repassivate (heal) when the pitting potential is increase.

The increase of the passive current density for the film resistance is suggesting the presence of a protective homogeneous layer on the steel surface. S2+MFP lead to the anodic formation of a passive layer which contributes to the decrease of chloride aggressiveness. A drop in

polarization resistance is an indication of reaching the critical chloride limit [Trejo and Pillai, 2004 and Qian et al., 2008] [31,32].

Perhaps a longer exposure time of MFP in the solution S2 was needed to increase the pitting resistance of the metal. At higher chloride concentrations of reference specimen S2, the pitting potential E_{pit} decreased to be -400 mV vs. SCE, and the hysteresis loop did not close. The results of E_{pit} are shown in Table 5. This is an indication of the breakdown of the passive film and that the metal was not able to repassivate (was not able to heal) at these chloride concentrations. This behaviour can be explained by the competitive action of both Cl^- and OH^- ions in the solution [Naceur et al, 2007] [33].

3.2.5 The charge transfer and film resistance

Figure 12 and Figure 13 show an increase in the charge transfer resistance (R_{ct}) and film resistance (R_f) for all inhibitor more than the reference. However, R_f is equal to zero in Ref steel due to absence of inhibitors even with and without of Cl^- ions in the solution, this behaviour may be due to the time (8days) no sufficient for formation of film on the surface of steel. The order of inhibition when immersed in S1 is: AMA >CNI >MFP >Ref steel according to the values of R_{ct} , this meaning that AMA is more active in absence of chloride. The order of inhibition is: CNI >AMA >MFP >Ref steel according to the values of R_{ct} and R_f when immersed in S2, this meaning that CNI is more active in presence of chloride. Basically, the passive film has a higher resistivity with CNI, AMA and MFP than the reference in pore solution S2 due to competition between chloride and the film of inhibitors which act as mechanical barrier against corrosion. MFP seems slightly efficient in simulated pore solution and slightly lower with NaCl.

3.2.6 Surface analysis with SEM

a). SEM of carbon steel in S2+MFP

The SEM shows that the pitting was observed on the sample Figure 14b. The brighter surface in SEM microphotographs exhibit pits that appeared darker in optical microphotographs. The pits appeared to occur only on sharply faceted grains. This indicates the accumulation of salts of phosphorus, chloride and calcium in the pits. The cracks have higher phosphorus content and exhibited the deposition of corrosion products.

b). SEM of carbon steel in S2+AMA

In figure 14c the SEM observations show the presence of a great amount of corrosion products like balloons swell and spread over the entire layers of the film surface.

It is suggested [Smialowska et al.1985 and 1981] [23,24] that the presence of chlorides in the solution changes the composition, thickness, and density of the passive film. Some author's report that the film formed in the presence of chlorides becomes thicker, but more porous and hydrated, losing its protective character [Jamil HE et al. 2005] [34].

The negatively charged ions (chloride ion) could reflect an interaction with the protonated amino groups.

c). SEM of carbon steel in S2+CNI

In figure 14d the SEM observations show the presence of a white precipitate formed over surface. This precipitate was analysed using EDS (X-ray spectroscopy) and found to be predominantly calcium and oxygen, suggesting that it is most likely $\text{Ca}(\text{OH})_2$. However, full protection depends greatly on the concentration of aggressive ions such as the chloride ion. The free chloride concentration in the pore solution admixed with CNI decreased and the OH^- content increased with the time of aging.

CNI is highly soluble in neutral solution. However, in solutions of very high pH value the concentration of Ca^{2+} ions is strongly limited by the solubility product of $\text{Ca}(\text{OH})_2$. The presence of CN in the pore solution causes part of its Ca^{2+} ions to react with the OH^- ions in the solution to precipitate calcium hydroxide [Li et al, 2000] [5].

3.3 Corrosion behaviour in solution extract of blended cement.

3.3.1 Results of Carbon Steel Immersed in Solutions Extract of blended Cement Admixed with AMA

In the recent years, there are few studies using AMA in advanced types of blended cement concrete. So this new study focused only on using ethanolamine in extract pore solution of blended cement.

a). Open circuit potential

Figure 15 shows the open circuit potential tests for carbon steel samples immersed in solution extract of cement without chloride (EC) and solution extract of cement with chloride 35 g/l added to the solution (ECC). After 8 days the rest potentials E_{OC} are almost constant with time respectively around -250 mV for the EC+AMA and -330 mV for EC. According to ASTM (C876) the rebars in EC+ AMA are probably passive. These results indicate adsorption of passive film on the iron surface.

For ECC, after eight days, the rest potential values are higher until 6 days then decrease. This means that the corrosion conditions are in risk range.

b). Corrosion current evolution

The corrosion currents are illustrated in Figure 16. After addition of inhibitor, the data shows lower corrosion currents with time and after 8 days the corrosion current range is from 4.5 to 3.9 $\mu\text{A}/\text{cm}^2$ for EC+AMA. It is to be noticed that this corrosion current constant with tendency of steel to corrode, which could be considered as an efficiency indicator for the inhibitor treatment according to RILEM studies [Andrade et al. 2004] [21]. In case of EC and EC+AMA the corrosion activity is constant. In case, of extract solution ECC without inhibitor, under amount of chlorides 35 g/l gives corrosion activity increase with time and those obtained from extract solution with inhibitor ECC+AMA decrease due to presence of amino inhibitors and this results agree with [Qian et al, 2008] [32]. The ECC behaviour can

be explained by lowering of pH by competitive action of both Cl^- and OH^- ions in the solution (see equation [8.3]).

c). EIS measurements in pore solution

Figure 17 shows a Nyquist plot of the impedance for carbon steel samples immersed in solution extract of cement with and without chloride in presence of AMA.

The electrical parameters obtained through fitting EIS data, using the electric equivalent circuit $R(\text{QR})$ and $R_{\text{el}} + C_f / (R_f + C_{\text{dl}} / R_{\text{ct}})$, are listed in Table 6. From these diagrams low values of C_f and C_{dl} are recorded. The increase in the sum of the charge transfer resistance and the film resistance ($R_{\text{ct}} + R_f$) was observed was adding of AMA.

For ECC, an increase in the sum of the charge transfer resistance and the film resistance ($R_{\text{ct}} + R_f$) was observed with AMA. It is remarkable that the film capacitance of AMA increased by about three times from the beginning in EC of the experiment AMA (C_f 27.6 $\mu\text{F}/\text{cm}^2$) until a chloride concentration in the solution ECC of 35g/l (C_f 80 $\mu\text{F}/\text{cm}^2$). AMA has great corrosion protection ability although it induced more chloride ion into the OPC concrete than BCC. This corrosion protection might be greatly attributed to the organic part in AMA around the rebar. The low frequency portion of the impedance spectra decreases in solution extract of cement in presence of chloride ion in the solution.

Conclusions

From the results presented in this paper it can be concluded that:

- Calcium nitrite (CNI), sodium monofluorophosphate (MFP) and ethanolamine (AMA) based inhibitors showed reductions in the overall rates of corrosion after the inhibitive treatments.

- 560 ▪ In alkaline solution with or without chloride, the CNI steel sample is more resistant than
561 carbon steel alone and causing passivation of steel in concrete. Thus, a dense and
562 protective layer is formed.
- 563 ▪ The laboratory study in simulated pore solution proved that all tests in simulated concrete
564 pore solution proved that the amino alcohol inhibitor can reduce corrosion: the most
565 important parameter is the ratio of inhibitor/chloride concentration,
- 566 ▪ if the steel reinforcement is heavily corroded the critical concentration ratio is strongly
567 dependent on the steel surface conditions: after the initiation of corrosion this ratio must
568 be quite high (e.g. 1:1) for the retardation of corrosion and if the steel is heavily corroded
569 complete repassivation is practically impossible,
- 570 ▪ the efficiency of the inhibitor in solution with higher pH (simulated concrete pore solution
571 without chlorides) cannot be exactly assessed, because the inhibitor shows a buffering
572 effect,
- 573 ▪ passivation due to the inhibitor is reached by the formation of an adsorbed layer on the
- 574 ▪ steel surface,
- 575 ▪ when the critical concentration ratio is not reached, the layer is partly destroyed, and the
576 corrosion damage is rather localized (localized corrosion spots can be relatively deep),
- 577 ▪ when the stabilization of the passive state is reached due to the inhibitor and subsequently
578 the concentration of the inhibitor is reduced, the initiation of corrosion might reoccur (the
579 ratio of concentrations inhibitor/Cl⁻ is critical also in such cases),
- 580 ▪ the sooner the inhibitor is introduced after corrosion propagation the more effective it is,
- 581 ▪ it can be expected that the long-term concentration of the inhibitor near the reinforcement,
582 which may decrease over time due to leaching and evaporation, is a crucial parameter for
583 the effectiveness of the inhibitor as part of a repair strategy

- $\text{Na}_2\text{PO}_3\text{F}$ hydrolyses into the pore solution simulating the concrete to form phosphate and so anodic formation of passive layer contributes to the decrease of chloride aggressiveness.
- The corrosion currents measured for solution extract of blended cement were significantly higher than those obtained at the same chloride concentration in the mortar and pore solution. It was found that the corrosion currents of carbon steel embedded in mortar immersion in NaCl at 3, 5%, would decrease due to the decrease in the degree of pore saturation PS after 28 days. Regardless in the presence of chloride content, the corrosion current was as low as $1, 5 \mu\text{A}/\text{cm}^2$.
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