

Research Article

Effect of Organic Inhibitors on Chloride Corrosion of Steel Rebars in Alkaline Pore Solution

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The inhibition properties of aspartic and lactic acid salts are compared with nitrite ions with regard to their effect on critical chloride concentration. The tests were carried out on carbon steel specimens in simulated pore solutions with initial pH in the range of 12.6 to 13.8. The critical chloride concentrations were estimated through multiple specimen potentiostatic tests at potentials in the usual range for passive rebar in noncarbonated concrete structures. During tests, chloride ions were progressively added until all specimens showed localized attack, obtaining cumulative distribution curves reporting the fraction of corroded specimens as a function of chloride concentration. The presence of the organic inhibitors on the passivity film was detected by IR spectra. The results confirm that 0.1 M aspartate exhibits an inhibiting effect comparable with nitrite ions of the same concentration. Calcium lactate does not increase critical chloride concentration; however it appears to promote the formation of a massive scale, reducing the corrosion propagation.

1. Introduction

The use of corrosion inhibitors as chemical admixtures during concrete mixing would be a simple and cost-effective solution for increasing concrete structures durability. However, so far the only inhibitor with demonstrated effectiveness in preventing chloride corrosion on real structures is calcium nitrite [1–4]. Recently, some literature works report the results of research on the use of salts of organic acids as an alternative solution to nitrites. In previous works [5, 6], the effect of chloride/hydroxyl ions ratio on the inhibiting properties of aspartate ions was evaluated by means of cyclic voltammetry. Furthermore, long-term tests in reinforced concrete pointed out the ability of lactate ions to retard corrosion damage on steel bars [7].

Tests in simulated concrete pore solutions are widely adopted for experimental study of chloride corrosion. This approach does not reproduce the metal/hydrated cement paste interface and its buffering capacity, which is significant in pitting initiation, as stressed by Page [8]. However, it allows cheap and rapid testing suitable for the screening of a large number of substances in a well-controlled environment.

Furthermore, a significant amount of data can be collected to match the statistical nature of pitting. Potentiostatic polarisation tests utilizing a step-by-step increase in chloride concentration to define the critical chloride content were previously successfully adopted on commercial admixture inhibitor [3].

This paper reports on multiple specimen potentiostatic tests comparing the inhibition properties of aspartate and lactate with nitrite ions. IR spectra were also carried out in order to highlight the presence of organic adsorbed species on the passivity film of the specimens. The effect of pH and chloride concentration on the pitting initiation was evaluated.

2. Experimental Details

2.1. Potentiostatic Tests. The tests were carried out on ferritic-pearlitic carbon steel. Disks of 5 mm height were cut from 10 mm diameter bar. The electrical junction was realized through a steel wire welded on the backside of the specimen, placed in an insulating PTFE sheath. Afterwards, the lateral surface and electric connection were embedded by casting with two component polyurethane resins. Finally,

the exposed surface was grinded with emery paper up to 2400 grit.

The tests were performed at room temperature in aerated saturated solution of calcium hydroxide. The pH was maintained between 12.6 and 13.5 by addition of sodium hydroxide to limewater. The inhibitors were directly added into the solution at concentrations of 0.1 mol/L for calcium lactate, 0.1 and 0.5 mol/L for sodium aspartate, and 0.1 and 1 mol/L for sodium nitrite. The concentrations were chosen on the basis of previous results [7].

The pH of test solutions was verified by potentiometric titration, by using a glass electrode.

During test, six specimens were immersed in a 2 L polypropylene cell and polarized at 0 mV with respect to calomel reference electrode (SCE) placed in the center of the cell. A mixed metal oxide activated titanium wire counter electrode on the cell bottom ensured the uniform distribution of current. The anodic current flowing through each specimen was monitored as ohmic drop on shunt resistance.

Initially, the specimens were prepassivated in the alkaline solution, without chlorides. After 70 or 90 hours, NaCl was added to the solutions in an amount proportional to the molar content of hydroxyl ions, that is, 0.47, 1.17, and 3.7 g/L for pH 12.6, 13, and 13.5, respectively. Further additions of the same chloride quantities were performed every 48 hours until all specimens showed localized attacks. The breakdown of passivity film was detected through the sudden increase of the ohmic drop on the shunt resistance. After the initiation of corrosion, the specimen was removed from the solution and the test continued on the remaining passive specimens in order to obtain the cumulative distribution curve of critical chloride content, that is, the fraction of specimens showing pitting corrosion related to the chloride versus hydroxyl ratio. The specimens were observed after the tests to confirm localized corrosion initiation.

2.2. Fourier Transform Infrared Spectroscopy. Fourier Transform Infrared Spectroscopy (FTIR) was performed on specimens polarized at 0 mV versus SCE in saturated $\text{Ca}(\text{OH})_2$ + NaOH at pH 13.5 solutions in the absence of inhibitors, in the presence of 1 M NaNO_2 , 0.1 M calcium or sodium lactate, and 0.1 M or 0.5 M sodium aspartate. The specimens were passivated for 90 hours. After exposure, the specimens were extracted from the solution and dried with warm air just before the test. Reflectance measurements were carried out using a Bruker Tensor 27 FTIR spectrometer equipped with ATR (attenuated total reflectance) device. Spectra were collected between 600 and 4000 cm^{-1} .

3. Results and Discussion

3.1. Potentiostatic Tests in Absence of Inhibitors. Figure 1 shows cumulative distribution curves of corroded specimens as a function of chloride concentration. In the absence of inhibitor, the critical chloride concentration, which significantly promotes pitting, increases with alkalinity. At pH 12.6 and pH 13, all the specimens showed localized corrosion initiation even at chloride concentrations as low as 0.02 and 0.06 mol/L, respectively.

At pH 13.5, the critical chloride content rises up to 0.7 mol/L. The distribution curve slightly shifts to higher chloride content for prolonged passivation time, from 70 to 90 hours.

The appearance of specimens extracted from the testing cell after initiation of localized corrosion shows a large amount of corrosion products (Figure 2(a)). The presence of several pits on the surface was evidenced after pickling in diluted hydrochloric acid inhibited with 3 g/L hexamethylenetetramine (HMTA) (Figure 2(b)).

Hausmann [9] and Gouda [10] described the critical content of chloride for localised corrosion in terms of chloride/hydroxyl ion molar ratio, according to the general law

$$\frac{[\text{Cl}^-]}{[\text{OH}^-]^n} = k, \quad (1)$$

The molar concentration ratio in equation reflects the competitive action between chloride and hydroxyl ions in the process of passive film rupture and reformation during pitting initiation. Hausmann reported k values for simulated alkaline pore solutions in the range 0.5–1.08 with $n = 1$. Gouda fixed the parameters at values, respectively, of $n = 0.8$ and $k = 0.3$. Later work confirmed k values between 0.25 and 0.8, always assuming $n = 1$ [11–17]. The role of critical chloride-hydroxyl ratio was confirmed in previous experimental works by means of cyclic voltammetry [5, 6], which determined values $n = 1$ and $k = 0.6$.

Figure 3 summarizes the results in terms of cumulative frequency of corroded specimens as a function of chloride to hydroxyl ions ratio. Different populations are evidenced as a function of pH. This fact can be ascribed to the features of the step-by-step potentiostatic tests. At high pH, the critical chloride concentration increases so much so that to initiate localised attack a longer testing time is required, during which passivation of the specimens' surface continues, determining a further raise of critical chloride concentration. Thus, in order to evaluate the effect of inhibitors on chloride concentration, a single critical chloride to hydroxyl ion ratio cannot be used for evaluating the results and the pH of the solution must be also considered.

From the experimental cumulative distributions of corroded specimens (Figure 3), the chloride content required to initiate the pitting on 50% of specimens was derived ($C_{0.5}$). Such chloride content is shown in Figure 4 as a function of pH.

3.2. Effect of Inhibitors. Figure 5 reports the curves in solution with nitrite ion addition. The chloride concentration value where pitting initiation appears is strictly dependent upon the concentration of nitrite ions. A slight inhibition effect can be noticed for 0.1 M sodium nitrite and 70-hour passivation but the probability of pitting initiation is substantially in the same range as in reference solution.

However, such nitrite concentration is below the range reported in the literature [11, 18–23] for the composition of pore solutions in chloride-contaminated concrete with significant nitrite additions. The inhibition effect is far more evident at 1 M concentration with 90 hours prepassivation.

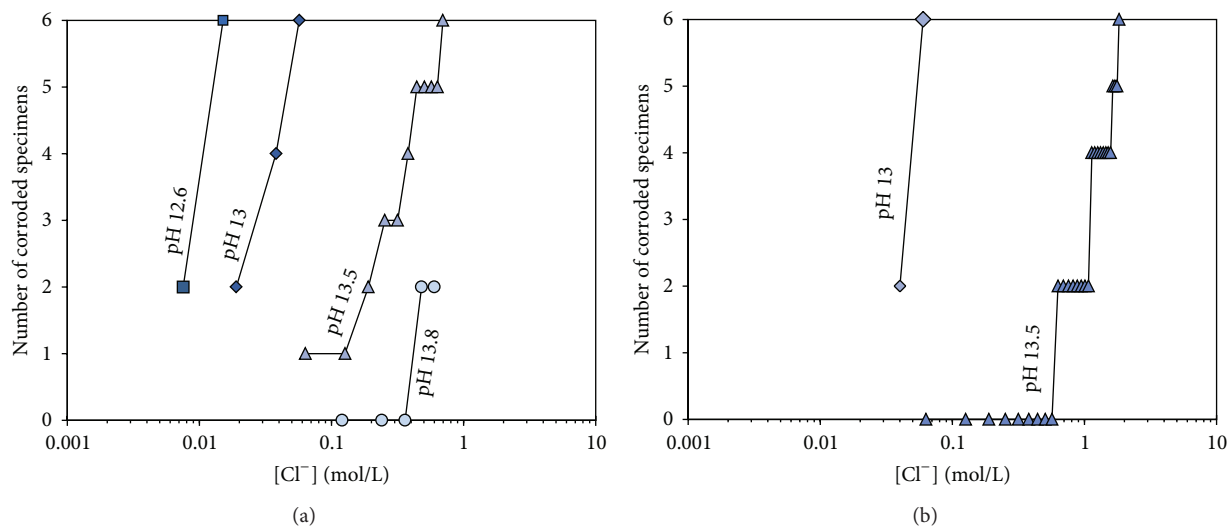


FIGURE 1: Number of corroded specimens as a function of chloride addition during potentiostatic test in lime solutions without inhibitor; (a) 70 h and (b) 90 h of passivation.

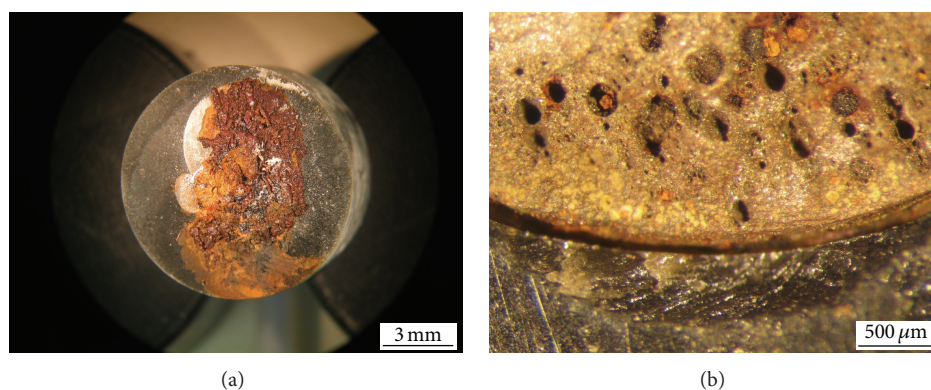


FIGURE 2: (a) Specimen extracted from the cell after pitting initiation during potentiostatic polarization test; (b) details of the surface showing pits.

The results in solutions with 0.1 mol/L calcium lactate at pH 13.5 are shown in Figure 6. The chloride content, which promotes pitting initiation, is almost comparable with the reference solution without inhibitor. The results of the test in solution containing sodium aspartate are shown in Figure 7. Although the chloride concentration that promotes localized corrosion on all specimens does not change with respect to the reference solution at pH 13.5, an effect can be evidenced at 0.1 M concentration and 70-hour passivation despite the lower pH, equal to 13.2. At 0.5 M concentration, the curve slightly shifts to the left compared to the curve at 0.1 M. The effect of inhibitors on the critical chloride content, $C_{0.5}$, is summarized in Figure 8 as a function of pH and passivation time. A real strong increase of the chloride critical concentration is evident only for nitrite ions in high concentration where the pitting of 50% of the specimens was not reached even after addition of 2 M of chlorides. Aspartate ions seem to slightly increase $C_{0.5}$, while on the contrary lactate ions do not show any such effect.

3.3. Mechanism of Inhibition. The behaviour of the three substances considered in the experimental research can be analysed on the basis of the pitting theory and the features of FTIR spectra.

Figure 9 illustrates the typical active/passive anodic polarization curve of carbon steel in alkaline media. In absence of chlorides the steel maintains its passive state until, over a threshold potential, the oxygen evolution takes place owing to water decomposition. In the presence of chloride ions over a critical concentration, on the steel localised corrosion occurs at pitting potential. Pitting potential decreases as the chloride content rises.

The polarization potential of potentiostatic tests is in the passivity range. This value was chosen because it approaches the open circuit potential of passive rebar in aerated uncarbonated concrete.

Many authors evaluated the pitting potential for rebar in concrete or pore solutions, but as underlined by Castellote et al. [24], the obtained values are very different. The reasons

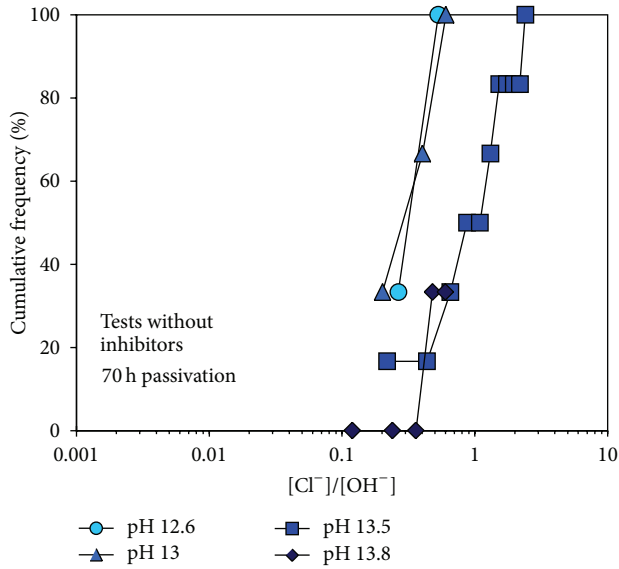


FIGURE 3: Cumulative frequency of corroded specimens at different pH as a function of chloride-hydroxyl ratio.

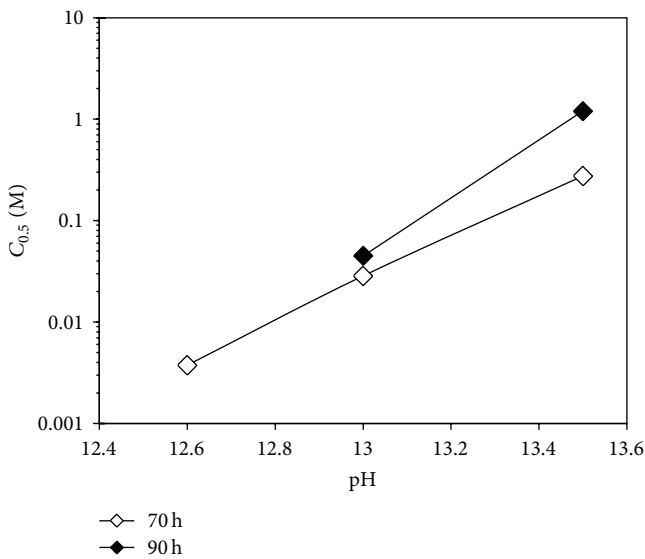


FIGURE 4: Effect of pH on critical chloride content during multispecimen potentiostatic tests.

are due to the technique employed for the pitting potential determination. For instance, it could be noticed that potentiostatic and galvanostatic tests give lower threshold values than potentiodynamic tests.

The adopted potentiostatic technique does not purport therefore to determine precisely the pitting potential, but only to compare with a method multisample the effect of inhibitors in solution on the resistance of the film to different levels of chlorides.

In the considered test conditions, pitting initiation becomes possible when the pitting potential falls below the imposed potential. The current registered through each specimen during the potentiostatic test has the typical behaviour

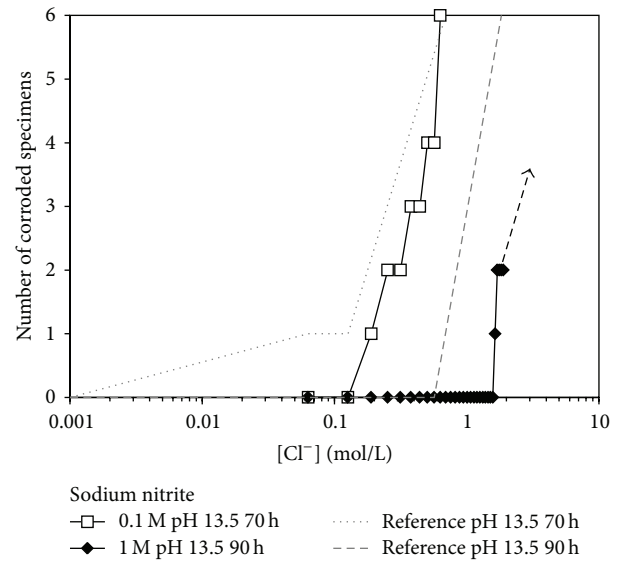


FIGURE 5: Number of corroded specimens as a function of chloride addition during potentiostatic test in solutions with sodium nitrite.

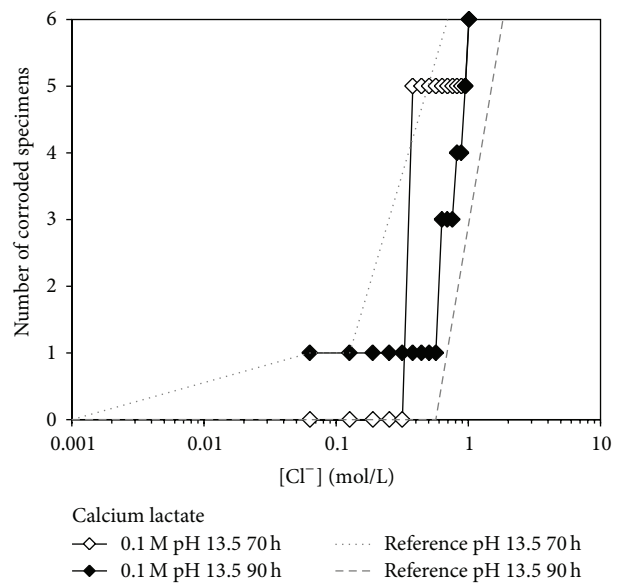


FIGURE 6: Number of corroded specimens as a function of chloride addition during potentiostatic test in solutions with calcium lactate.

shown in Figure 10. When the specimen is polarised, the current suddenly increases but then decreases rapidly to reach a very low value, corresponding to the passivity current. The mechanism commonly assumed for pitting initiation is the competitive chemisorption of chlorides and hydroxyl ions on passive film [25]; the higher the chloride content the higher the probability for substitution of Cl⁻ to OH⁻ ions, in the outer layer of passive film. If chlorides substitute OH⁻ group in a sufficient number of adjacent sites, the rupture of the passive film can occur with formation of embryo pit. This pit is metastable and hydroxyl ions and dissolved oxygen can restore the protective film on the inner

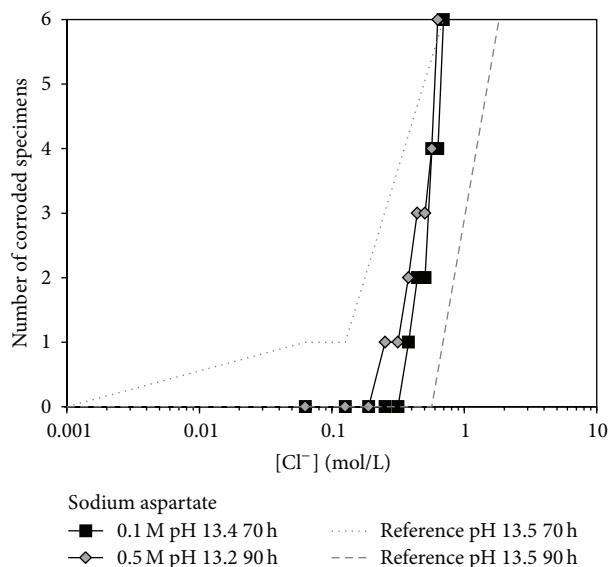


FIGURE 7: Number of corroded specimens as a function of chloride addition during potentiostatic test in solutions with sodium aspartate.

surface of embryo pit, which thus does not reach a stable propagation. On the contrary, the pit propagates by occluded cell mechanism and consequently repassivation gradually becomes less probable, because of acidification and high concentration of chlorides. The formation and repassivation of metastable pits are evident in the current versus time graph as spikes in the current that do not reach the threshold current value corresponding to specimen failure. Finally, once the pitting starts to propagate by the occluded cell mechanism, the current increases.

Corrosion inhibitors can act during one or more of the different stages of pitting initiation and propagation, by stabilizing the passivity state and increasing the critical chloride concentration to have embryo pitting initiation, by increasing the kinetic of repassivation of embryo pit or by decreasing the propagation rate of the initiated pit.

3.4. FTIR Spectra. Fourier Transform Infrared Spectroscopy (FTIR) was performed in order to evidence the formation of compounds on the surface, promoted by inhibitors. Figure 11 reports the FTIR spectrum of polished steel compared to the spectrum of steel passivated for 48 hours, at 0 V versus SCE, at pH 13.5. The two spectra are superimposable, with the exceptions of a broad band between 3500 and 3000 cm^{-1} , a small band near 2600 cm^{-1} , and a group of peaks between 1586 and 1552 cm^{-1} , only observed on the passivated specimen.

The broad band is in the range of the stretching frequency of the $-\text{OH}$ groups of the different allotropic forms of FeOOH (α -goethite, β -akaganeite, γ -lepidocrocite, and δ -feroxyhyte) [26].

The passivity film present on carbon steel in pore solution was studied in previous works using cyclic voltammetry [5–7]. The peaks on the voltammogram indicated that film formation proceeds by initial oxidation of Fe to Fe^{II} in the form of $\text{Fe}(\text{OH})_2$; this reaction is partially reversible.

The value of the peak current associated with this reaction remained constant with increasing of the number of voltammetry cycles, which indicates that the $\text{Fe}(\text{OH})_2$ film did not increase. The $\text{Fe}(\text{OH})_2$ film is further oxidised to different species depending on the environment and the potential scan rate. [27, 28]. In the test conditions adopted in the considered works, the most probable oxidation product is lepidocrocite, γ - FeOOH . Joiret et al. [29] emphasized the magnetite (Fe_3O_4) formation. Following Andrade et al. [30] the external layer is constituted by magnetite Fe_3O_4 partially oxidised to γ - FeOOH . γ - FeOOH can subsequently dehydrate to give Fe_2O_3 . Electrochemical Impedance Spectroscopy confirmed the double nature of the passivity film [23, 31]. Montemor et al., using XPS analysis, reported that the outermost layers of passive films were mostly composed of FeOOH (Montemor et al.) [32].

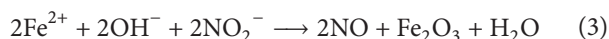
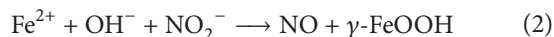
FTIR spectra analysed only the external surface of the passivity film. It is reasonable to think that the peak in the range 3500 \div 3000 cm^{-1} is due to a mixture of the polymorphic forms of FeOOH present on the external side of the film.

The other peaks are not typical of these hydroxides. Spectra with peaks in the range of 1650 and 1540 cm^{-1} were observed on specimens covered by amorphous or crystalline $\text{Fe}(\text{II})$ and $\text{Fe}(\text{III})$ hydroxides and carbonates, with different stoichiometric ratios, called green rust [33].

The peaks at 1430, 1785, and 2530 cm^{-1} are characteristic of calcium carbonate, which can form by reaction of $\text{Ca}(\text{OH})_2$, incorporated in the passivity film [27, 28], with atmospheric CO_2 . Ghods et al. determined by means of XPS that microsize calcium hydroxide and/or calcium carbonate particles are present on the film surface and remained also after the specimens were removed from the calcium hydroxide solution and dried [34].

In Figure 12 the FTIR spectrum registered on the specimen passivated at 0 V versus SCE in alkaline solution added with 1 M sodium nitrite is compared with that obtained in solution without inhibitor. The absence of FeOOH signals in the nitrite-containing sample is evident.

The inhibitive action of nitrite ions depends on their reaction with Fe^{2+} ions according to the following reactions:



In the literature there is unanimous accord on the effect of nitrite in accelerating the oxidation reaction of the $\text{Fe}(\text{II})$ to $\text{Fe}(\text{III})$, but there are conflicting data about the composition of the passivity film in the presence of nitrite. According Giréienė, the outer layer of the film consists of FeO . AFM analysis demonstrated that the film formed in presence of nitrite ions is less porous and more compact than those formed on $\text{Ca}(\text{OH})_2$ without inhibitor [35].

FTIR spectra seem to confirm the decrease of $-\text{OH}$ groups in the outermost layer of the film, in the presence of nitrite.

Nitrite ions aid the formation of a stable passive layer even in the presence of chloride ions, because reactions (2) and (3) are faster than the transport of ferrous by means of a chloride

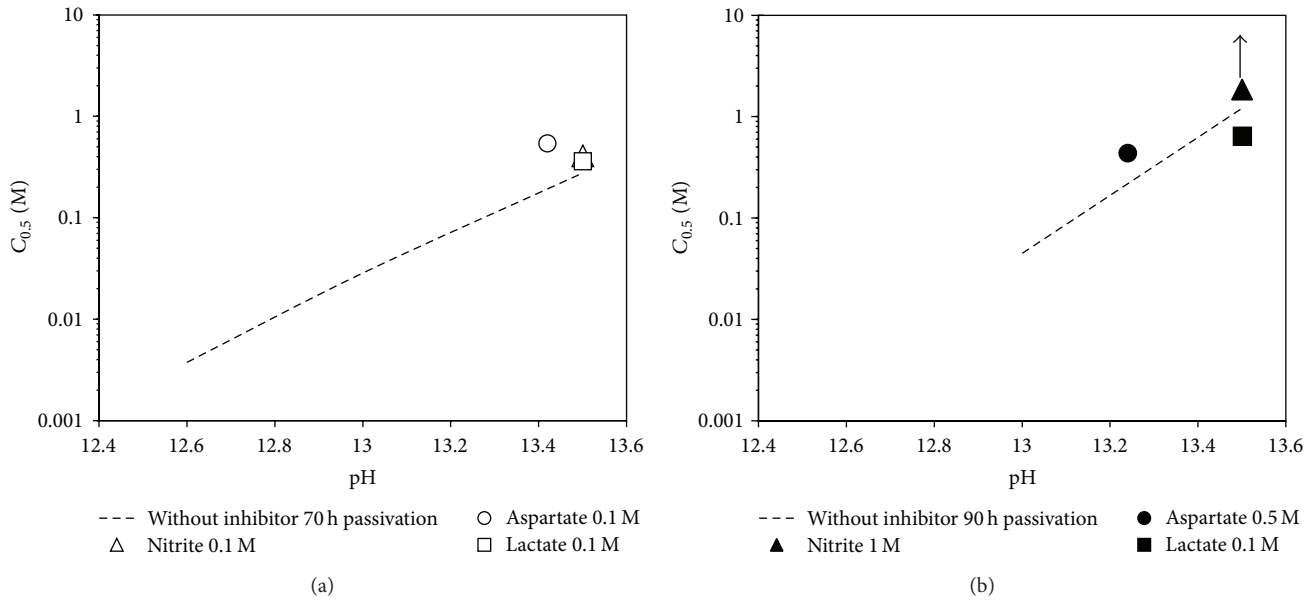


FIGURE 8: Effect of pH on critical chloride content during multispecimen potentiostatic tests (a) at 70 h of passivation and (b) at 90 h of passivation; $C_{0.5}$ was not reached in the case of nitrites.

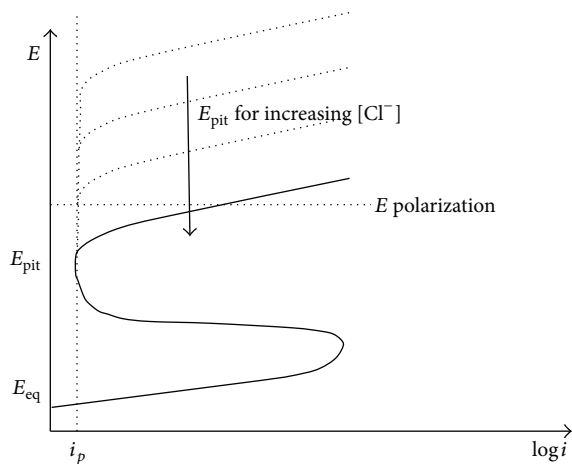


FIGURE 9: Example of polarization curves of carbon steel in alkaline solution as a function of chloride concentration.

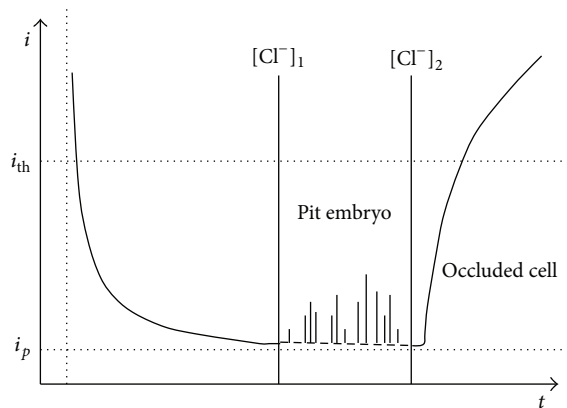


FIGURE 10: Effect of time and chloride concentration on pitting initiation.

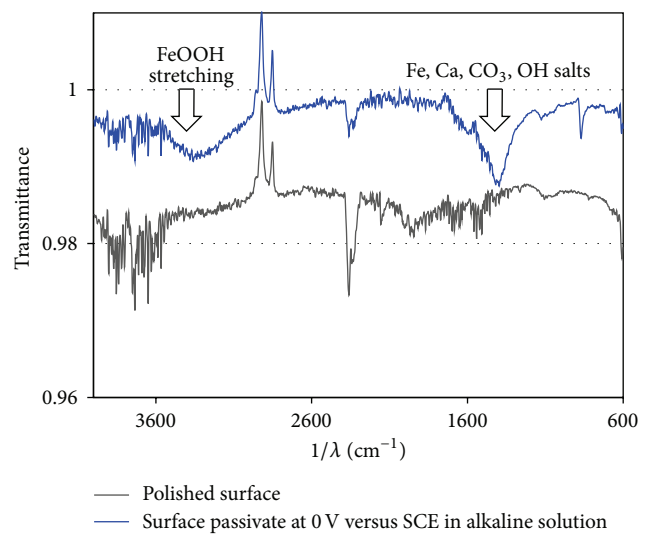


FIGURE 11: FTIR spectra of a polished specimen and a specimen passivated in solution at pH 13.5 and 0 V versus SCE.

ion complex formation [2, 5, 26]. However, full protection depends greatly on the concentration of chloride ion [5], and severe pitting may occur when insufficient quantity of inhibitor is used compared to the level of chloride in the concrete [3, 11].

Nitrite ions cooperate with hydroxyl ions to rebuild the protective film [5, 6], one nitrite and one hydroxyl ion being involved to counteract the chlorides. This effect is only operating during the nucleation period, before acidification caused by the occluded cell mechanism becomes too severe. After initiation, nitrite ions produce deep penetration of

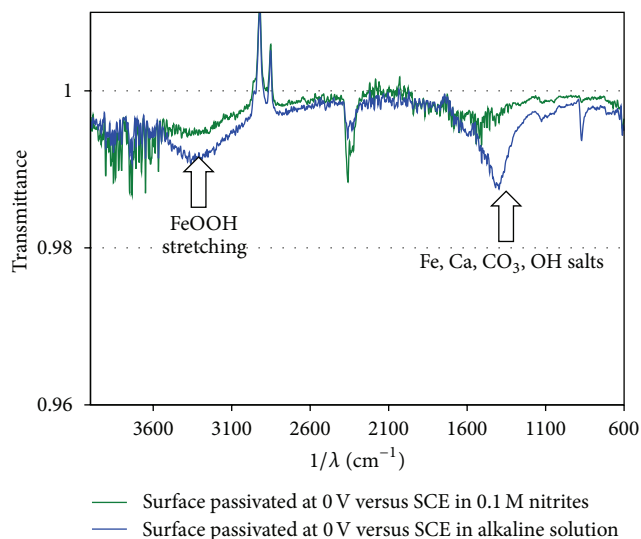


FIGURE 12: FTIR spectra of specimens passivated in solution at pH 13.5 and 0 V versus SCE without and with 0.1 M NaNO_2 .

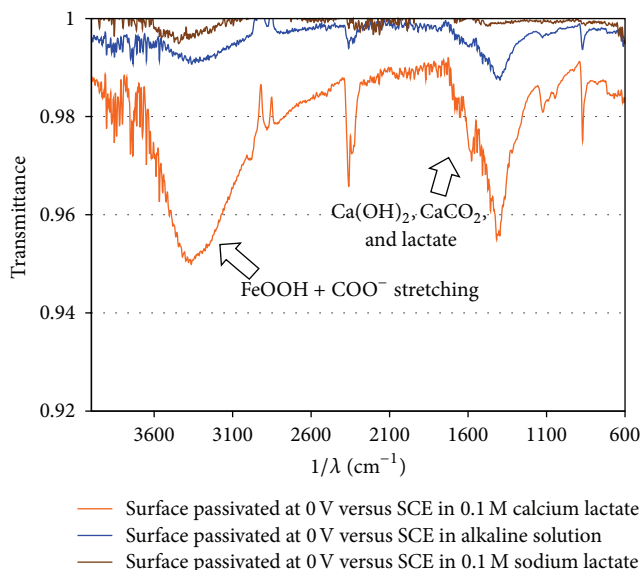


FIGURE 13: FTIR spectra of a specimen passivated in solution with and without calcium lactate 0.1 M or sodium lactate 0.1 M at pH 13.5 and 0 V versus SCE.

localised attack owing to their oxidizing character, contributing to the anodic process. Insufficient nitrite content with respect to chloride can therefore produce deeper penetration of localised corrosion; hence the well-known necessity to maintain a high concentration of nitrite ions in solution to preserve the steel from localised corrosion. Adverse effects due to insufficient concentration represent the main problem in the use of this inhibitor in concrete. Figures 5 and 8 show that inhibition by nitrite ions becomes evident when their concentration is comparable with hydroxyl ions concentration.

Figure 13 compares the spectrum obtained on a specimen passivated in solution with calcium lactate at pH 13.5 with the

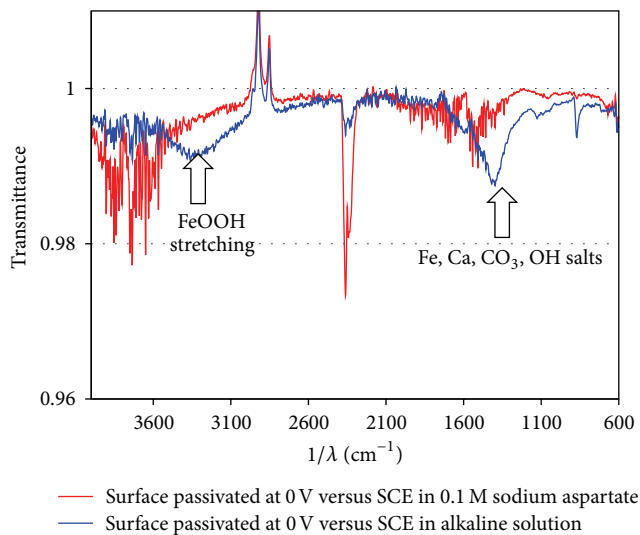


FIGURE 14: FTIR spectra of a specimen passivated in solution with and without sodium aspartate 0.1 M at pH 13.4 and 0 V versus SCE.

spectrum obtained in absence of inhibitor. After passivation, a clearly visible white scale covers the surface of the specimen. Both spectra show the presence of a broad peak at 3272 cm^{-1} and several well-defined peaks at 1576 , 1454 , 1417 , 1366 , 1315 , 1122 , 1042 , 855 , and 638 cm^{-1} . These latter peaks are characteristic of lactate, while the first one is characteristic of the stretching of the $-\text{OH}$ groups of both the iron oxide and the OH group of the organic acid. Such peaks overlap, giving a broad band. The spectrum confirms the presence, on the surface of the specimen passivated in alkaline calcium lactate solution, of a mixed composition film containing lactate ions. On the other hand, the presence of signals attributable to lactate ions is not evident in the spectrum when the samples are treated with sodium lactate instead of calcium lactate: the spectrum obtained in these conditions is essentially superimposable to the one recorded in the absence of inhibitor. This confirms that, as soluble calcium lactate is added, Ca^{2+} ions become supersaturated in the alkaline solution and precipitate in the form of a calcium hydroxide gel. No macroscopic adsorption effect is therefore evidenced for this inhibitor. Actually, infrared spectroscopy is not in itself an extremely sensitive detection technique, so that the presence of very small quantities of analyte would not be observed.

The above results demonstrate that lactate ions have no effect on pitting initiation, confirming previous works [5, 6]. On the contrary, long time tests carried out on concrete specimens [7] evidenced the possibility of lactate ions to slow down the pit propagation. Lactate ions do not contribute to the protectivity of the passive film, but their steric hindrance could reduce the contribution of the cathodic process and slow down the pit propagation. This effect is not visible in the electrochemical tests but becomes evident in long time exposure tests at the corrosion potential.

Figure 14 presents the FTIR spectra of specimens passivated in alkaline solution at 0 V versus SCE with and without sodium aspartate. Like the spectrum obtained in solution of

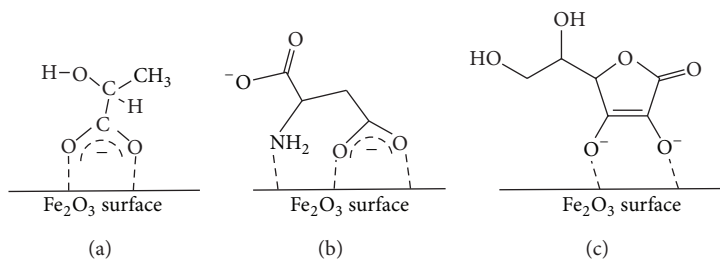


FIGURE 15: From left to right: lactate, aspartate, and ascorbate ions adsorbing on the iron oxide surface.

sodium nitrite, the IR spectrum in the presence of sodium aspartate did not show the peaks characteristic of Fe(III) oxide. However, contrary to nitrites, aspartate ions are not oxidizing.

The behaviour of aspartate ions can be interpreted by considering their chelating properties. Ormellese et al. [36] stated that organic acid salts act as inhibitors in pore solution by adsorption of carboxylic groups on the metal surface by the delocalised charge on the two oxygen atoms (Figure 15). Electron-donating groups, namely, hydroxyl in the case of lactic acid and amine for aspartic acid, favour this effect. However, steric hindrance penalizes their competition against chloride adsorption. Aspartic, however, is a weak bicarboxylic acid that can adsorb on the iron oxide by assuming an annular configuration and counteract chloride adsorption by negative charge repulsion (Figure 15).

In fact, Kalota and Silverman [37] demonstrated that, for the inhibiting properties of aspartic acid on iron, the fully ionised form is required in solutions above pH 10. They performed tests at pH values below the range of concrete pore solutions and showed that, in less alkaline solutions, aspartic acid stimulates corrosion by complex formation with iron ions. Thus, high pH is necessary to counteract the acidification taking place on the film surface in the presence of chloride ions during the first stage of pitting initiation; in fact, acidification moves the dissociation equilibrium of aspartic acid towards the undissociated form, which is unable to adsorb on the film.

Valek et al. [38] found a similar complex behaviour in evaluating the inhibition effect of ascorbic acid in alkaline media: the inhibition efficiency decreases with increasing acid concentration. The anion of this acid is known to form chelates through the hydroxyl groups of the lactone ring; hence it can be adsorbed onto the metal surface through formation of stable chelates with coordinatively unsaturated surface Fe ions (Figure 15). These authors discuss literature data and outline that an increase in the concentration of the complexing agent shifts its effect from inhibitive to stimulative one towards iron dissolution. Solubility of a complex is mainly determined by metal/ligand ratio, since for higher ratios sparingly soluble mono- or polynuclear complexes could be formed, while for lower ratios soluble complexes could be formed. They concluded that the increase in ligand concentration and the resulting decrease of the metal/ligand ratio in the near electrode layer create favourable conditions for soluble complexes formation, while at low concentration

insoluble chelates are formed [38]. Moreover, these authors hypothesized that the chelating action could stabilize the Fe(II) ions of the passive film, giving a much less soluble complex than the one formed by Fe(III) ions. Therefore, the chelating agent addition promotes thinner passive film, whereas the adsorption of molecules on the surface tends to block the adsorption of chlorides, extending the pitting initiation time. Similar behaviour has been assumed for the passive layer of steel in presence of EDTA [38]. It was suggested that EDTA supported dissolution of the barrier layer and hindered formation of the outer barrier because of its ability to chelate Fe(II) cations ejected from the oxide layer. On the other hand, EDTA adsorbs strongly on the oxygen vacancies at the barrier layer/solution interface, thereby effectively blocking the adsorption of Cl^- at the surface of the passive film. However, previous tests demonstrated that 0.28 mol/L of EDTA enhanced generalised dissolution of steel [39].

The hypothesis that aspartate creates a similar chelating complex adsorbed on Fe(II) oxide and a soluble complex with Fe(III) ions is in agreement with FTIR spectra. The potentiostatic results evidenced that this substance shows an inhibition effect in concentration 0.1 M, but its beneficial effect decreases by increasing its concentration to 0.5 M.

4. Conclusions

This paper studies the effect of the addition of lactic and aspartic acid salts on localized corrosion of passive rebars in alkaline simulated pore solution initiated by chloride ions. Potentiostatic multiple specimen tests were used to evaluate the time required for pitting initiation as a function of chloride content and pH, while FTIR spectroscopy allowed gaining further insight into the nature of the species constituting the passive film.

The effectiveness of these organic substances was compared with the well-known inhibiting properties of nitrite ions, and hypotheses have been put forward on the possible inhibition mechanisms.

Under test conditions considered in the research, the inhibition effect of 1 M nitrite concentration is evident, while at 0.1 M concentration there is only a slight effect. FTIR spectra confirm the effect of nitrite ions on the stability of the Fe(II) film and their inhibition mechanisms both on the initiation stage and on the kinetic of repassivation of metastable pits.

In the case of calcium lactate, FTIR spectra evidenced the presence of a massive scale constituted by calcium hydroxide gel incorporating lactate ions, shielding the specimen surface, and slowing down the pit propagation, though without effect on the critical chloride concentration.

Aspartate ions, on the opposite, appear to adsorb on Fe(II) oxide surface due to their chelating properties and exert their inhibiting properties through a negative charge repulsion by their nonadsorbed carboxylate group, effectively increasing the critical chloride content. This inhibitor is effective in concentration 0.1M, but its beneficial action decreases by increasing its concentration to 0.5 M.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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