

Study of Chloride Corrosion Organic Inhibitors in Alkaline Pore Solution

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(Received June 14, 2018; Revised September 05, 2018; Accepted September 05, 2018)

This paper compares the inhibition properties of aspartic and lactic acid salts with nitrite ions and their effect on critical chloride concentration. The tests were carried employing carbon steel specimens in saturated lime solution with varying pH in the range between 13 to 13.6. The critical chloride concentration was estimated through multiple specimen potentiostatic tests at potentials in the usual range for passive rebar in the alkaline concrete of atmospheric structures. During tests, chloride salt was added every 48 h until all the specimens showed localized attacks. The cumulative distribution curves, i.e. the number of corroded specimens as a function of the chlorides concentration was obtained. Furthermore, IR spectra were recorded for the evaluation of the presence of the organic inhibitors on the passivity film. The results confirmed the inhibitory effect of 0.1M aspartate comparable with nitrite ions, at a similar concentration. Addition of calcium lactate did not result in an increase in the critical chloride concentration. However, the formation of a massive scale containing the substance that could reduce the corrosion propagation was observed.

Keywords: Rebar, Localized corrosion, Corrosion inhibitors, Chloride, Pore solution

1. Introduction

The use of corrosion inhibitors as chemical admixtures during concrete mixing is cost-effective and a simple solution for common concrete practices. However, their effectiveness is yet to be demonstrated. Calcium nitrite is the only inhibitor that was able to prevent chloride corrosion on real structures [1-4], but even for this inhibitor, there are still doubts concerning washout in critical areas, such as cracks, to maintain the minimal concentration that ensures corrosion protection. Recently, some literature works report the results of research on the use of salts of organic acids as an alternative solution to nitrites. In a previous paper [5,6], the effect of chloride/hydroxyl ions ratio on inhibiting properties of aspartate ions was evaluated by means of cyclic voltammetry. Long-term tests in reinforced concrete pointed out the ability of lactate ions to retard corrosion damage on steel bars [7].

Tests in simulating 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, the approach allows economic and rapid testing

that is suitable for investigation 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 that consider a step-by-step increase in the chloride concentration to define the critical chloride content were previously successfully adopted on commercial admixture inhibitor by [3].

This paper reports on multiple specimen potentiostatic tests performed in order to compare the inhibition properties of aspartate and lactate with nitrite ions. IR spectra were also carried out in order to evidence 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 Procedure

The tests were carried out on a ferritic-pearlitic carbon steel. Disks were cut from 10 mm diameter bar, with 5 mm height. The electrical junction was realized through a steel wire welded on the backside of 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.

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The tests were performed at room temperature in aerated saturated solution of calcium hydroxide. The pH was adjusted 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 Mole/L for calcium lactate, 0.1 and 0.5 Mole/L for sodium aspartate, and 0.1 and 1 Mole/L for sodium nitrite. The concentration of organic compound is based on 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 respect to calomel reference electrode (SCE) placed in the center of the cell. A mixed metals 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 a shunt resistance.

Initially, the specimens were pre-passivated in the alkaline solution, without chlorides. After 70 or 90 hours, an amount of NaCl, salt was added to the solutions proportional to the molar content of hydroxyl ions i.e. 0.47, 1.17, 3.7 g/L for pH 12.6, 13, 13.5, respectively. Further additions increased the chloride content every 48 hours until all specimens showed localized attacks. The breakdown of passivity was detected through the suddenly 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, i.e. the number of specimens showing pitting corrosion related to the chloride addition. The specimens were observed after the tests to confirm localized corrosion initiation.

Fourier Transform Infrared (FTIR) Spectroscopy was performed on specimens polarized at 0 mV vs SCE in the test solution with 0.1M inhibitor for 48 hours. After exposure, the specimens were rinsed and dried with nitrogen just before the test. Measurements were carried out using a Bruker Tensor 27 FTIR wspectrometer. Spectra were collected between 400 and 4000 cm^{-1} .

3. Results

3.1 Multi-specimen potentiostatic tests

Fig. 1 shows the aspect of specimens extracted from the testing cell once localized corrosion initiates. Large amount of corrosion products can be noticed due to anodic polarization. The presence of several pits on the surface was evidenced after pickling in diluted inhibited hydro-

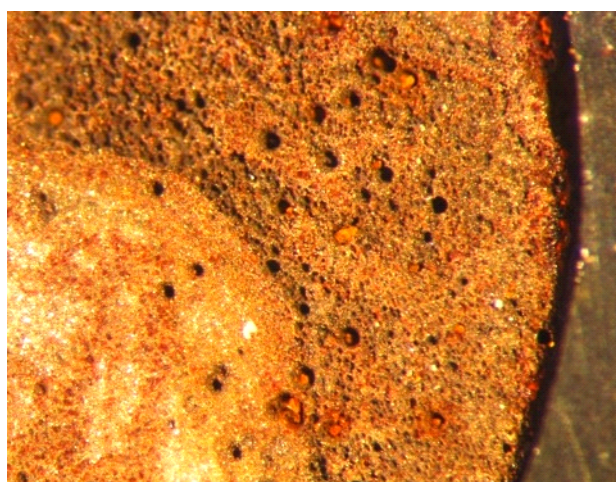
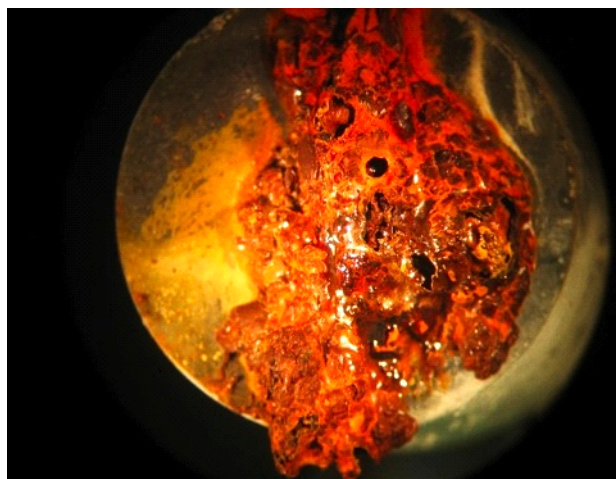


Fig. 1 Specimen extracted from the cell after pitting initiation during potentiostatic polarization test.

chloric acid.

Fig. 2a shows cumulative distribution curves of corroded specimens as a function of the chlorides addition into the solution. Without inhibitor, the critical chloride concentration, which promotes pitting significantly, increases with alkalinity. At pH 12.6 and 13, all the specimens showed localized corrosion initiation even at concentration as low as 0.02 and 0.06 Mole/L, respectively. At pH 13.5, the critical chloride content rises up to 0.7 Mole/L. The distribution curve slightly shifts to higher chloride contentment for prolonged passivation time, from 70 to 90 hours.

Fig. 2b reports the curves in solution with nitrite ions addition. The chlorides concentration, which promotes pitting initiation, is strictly dependent upon the concentration of nitrite ions. A slight inhibition effect can be noticed for 0.1 M sodium nitrite and 70 hours passivation but probability of pitting initiation is substantially in the same

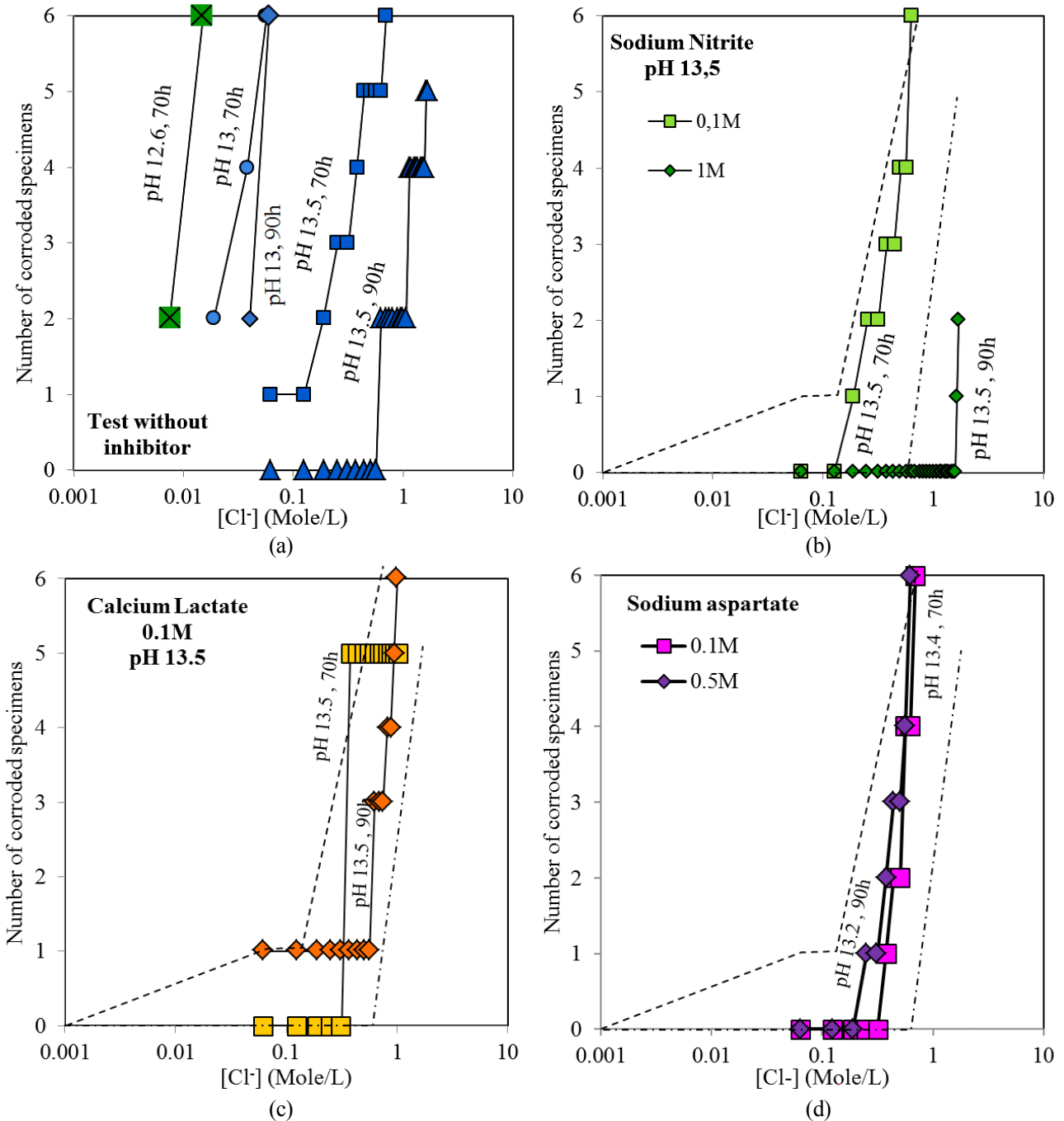


Fig. 2 Number of corroded specimens as a function of chloride addition during potentiostatic test: a) solutions without inhibitors at different pH and with different time of passivation; b) solutions with sodium nitrite; c) solution with calcium lactate; d) solution with sodium aspartate (dashed line is the reference curve at pH 13.5 with 70 hours pre-passivation; dash-dotted line is the reference curve at pH 13.5 with 90 hours pre-passivation).

range of reference solution. However, such nitrate concentration is below the range reported in literature [9,10] for the composition of pore solutions in chloride-contaminated concrete with significant nitrite additions. The inhibition effect is far more evident at 1M concentration with 90

hours pre-passivation.

The results in solutions with 0.1 Mole/L calcium lactate at pH 13.5 are shown in Fig. 2c. The chloride content, which promotes pitting initiation, is almost comparable with the reference solution without inhibitor.

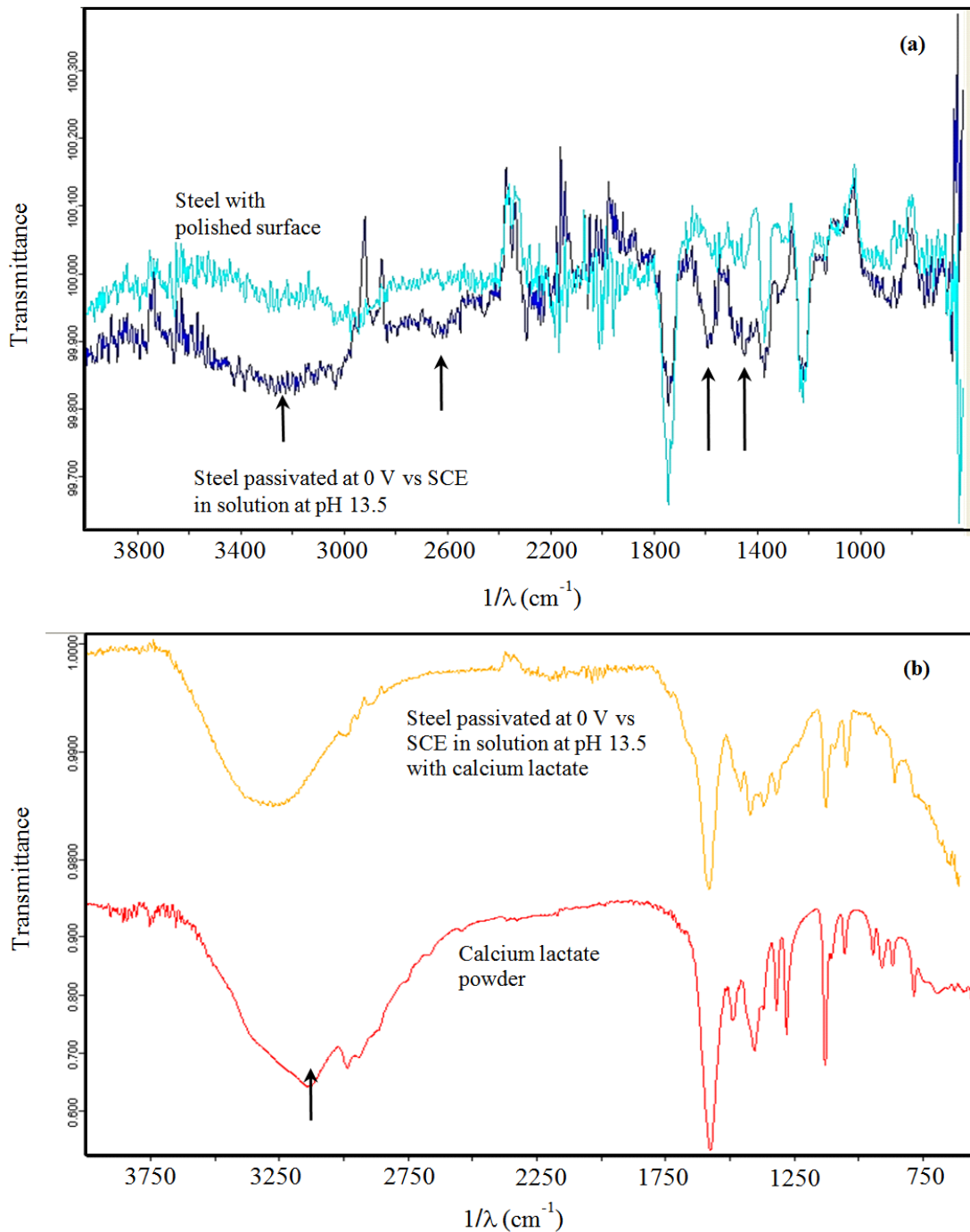


Fig. 3 FTIR spectra of (a) a specimen polished and a specimen passivated in solution at pH 13.5 and 0V vs SCE; (b) a specimen passivated in solution of calcium lactate 0.1 M and pH 13.5 at 0 V vs SCE and of the powder of calcium lactate.

The results of the test in solution containing sodium aspartate are shown in Fig. 2d. 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 hours passivation despite the lower

pH, equal to 13.2. At 0.5 M concentration, the curve shift to the left compared to the curve at 0.1 M.

3.2 FTIR spectra

Fourier Transform Infrared (FTIR) Spectroscopy was performed in order to evidence the formation of com-

pounds on the surface, promoted by inhibitors.

Fig. 3a reports the FTIR spectrum of polished steel compared to the spectrum of steel passivated for 48 hours, at 0 V vs SCE, at pH 13.5. The two spectra are superimposable with the exception of a broadband between 3500 and 3000 cm^{-1} , a small band in 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 (a-goethite, b-akaganéite, g-lepidocrocite and d-feroxyhite) [11]. It is reasonable to think that a mixed of these allotropic forms are present. The other peaks are not typically of these hydroxides. Spectra with peaks in the range of 1650 and 1540 cm^{-1} were observed on specimens covered by a $\text{Fe(II)}-\text{Fe(III)}$ and $(\text{OH})_e(\text{CO}_3^{2-})$ compounds, amorphous or crystalline, with different stoichiometric ratios, called green rust [12]. The peaks at 1430, 1785 and 2530 cm^{-1} are characteristic of calcium carbonate, which can form due to the reaction with the atmospheric CO_2 .

Fig. 3b compares the spectrum obtained on a specimen passivated in solution with calcium lactate at pH 13.5 with the spectrum of pure calcium lactate powder. After passivation, a clearly visible white scale covers the surface of specimen.

Both spectra show the presence of several well-defined peaks at 1576, 1454, 1417, 1366, 1315, 1122, 1042, 855 and 638 cm^{-1} . They only differ for the peak present on the passivated specimen at 3272 cm^{-1} that substitutes the two peaks of the lactate powder at 3133 and 2980 cm^{-1} . This zone of the spectrum is characteristic of the stretching of the $-\text{OH}$ groups of both the iron oxide and carboxylic group of the organic acids. Such peaks overlap, giving a broad band. The spectrum confirms the presence of mixed salt containing lactate ions on the surface of the specimen passivated in alkaline calcium lactate solution. On the specimens passivated at 0 V vs SCE in solution at pH 13.5 with either sodium nitrite or aspartate, the FTIR spectrum did not show the characteristic peaks of these substances. The spectra registered on these specimens are very similar to that obtained on the polished surface, without any passivation.

4. Discussion

Hausmann [13] and Gouda [14] described the critical content of chloride for localised corrosion in terms of the chloride/hydroxyl ion molar ratio, according to the general law

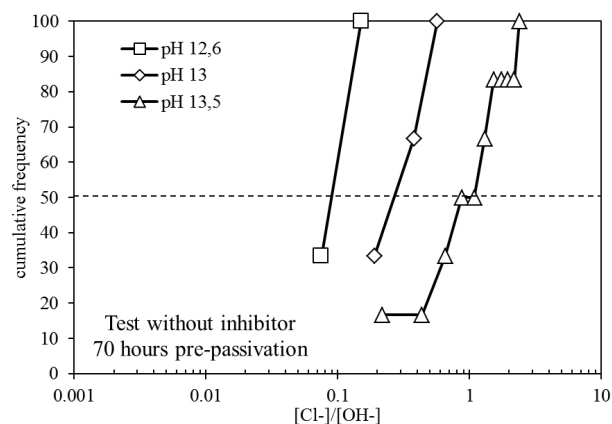


Fig. 4 Cumulative frequency of corroded specimens at different pH as a function of chloride-hydroxyl ratio.

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

The molar concentration ratio in equation represents the competitive action between chloride and hydroxyl ions in the process of passive film rupture and its reformation during pitting initiation. Hausmann reported k values for simulating alkaline pore solutions in the range 0.5-1.08 with unit exponent value of 1. Gouda fixed the parameters n and k equal to 0.8 and 0.3, respectively. Later work confirmed k values between 0.25 and 0.8, assuming a value of 1 for n [9,15-20]. The role of critical chloride-hydroxyl ratio was confirmed in previous experimental works by means of cyclic voltammetry [5,6]: the value of constants n and k was equal to 1 and 0.6, respectively.

Fig. 4 summarizes the results in terms of cumulative frequency of corroded specimens as a function of chloride to hydroxyl ions ratio. Three different populations as a function of pH remain. This fact can be ascribed to the characteristic of the potentiostatic tests adopted for evaluating the effect of the inhibitors, during which the chlorides were progressively increased. At high pH, the critical chloride concentration increases and longer testing time is required to initiate localised attack, during which passivation of the specimens surface continues. Actually, the effect of prolonged passivation periods can be observed in Fig. 2a. 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 of the potentiostatic tests and the pH of the solution must be considered.

From the experimental cumulative distributions of corroded specimens (Fig. 2) the chloride content required to initiate the pitting on 50% of specimens was derived ($C_{0.5}$).

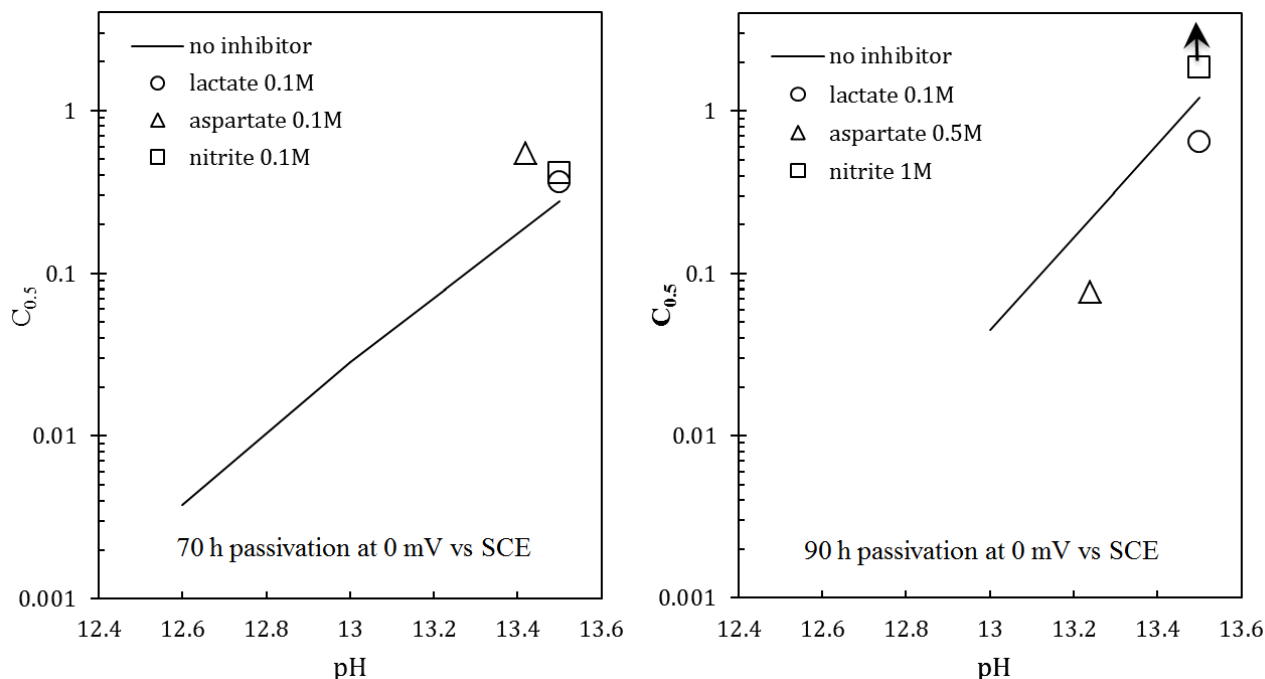


Fig. 5 Effect of lactate, aspartate on critical chloride content required to initiate the pitting on 50% of specimens during multi-specimen potentiostatic test with different passivation time.

Such chloride content is showed in Fig. 5 as a function of pH.

The effect of aspartate ions is complex. This substance shows an inhibition effect in concentration 0.1 M, but its beneficial effect vanishes by a further increasing of its concentration to 0.5 M. This behaviour can be interpreted by considering its chelating mechanism. Ormellesse et al. [21] stated that organic acid salts act as inhibitors in pore solution by absorption of carboxylic groups on the metal surface and the de-localised charge of the two oxygen atoms. Electron-donating groups, hydroxyl groups in the case of lactic acid and amine groups for aspartic acid, favour this effect. However, steric hindrance penalises their competition against chloride adsorption. Aspartic is weak bi-carboxylic acid that can adsorb on the iron oxide by assuming a ring configuration and counteract chloride adsorption. Furthermore, Kalota and Silverman [22] 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 that takes place on the film surface in the presence of chlorides ions during the first stage of pitting initiation, that move the equilibrium of dissociation of the aspartic acid to the un-dis-

sociated forms, which are not able to adsorb on the film.

Valek *et al.* [23] founded a similar complex behaviour evaluating the inhibition effect of ascorbic acid in alkaline media: the inhibition efficiency decreases with the increase of the concentration of the acid. The anion of this acid is known to form chelates through hydroxyl groups of the lactone ring, hence it can be adsorbed at the metal surface through formation of stable chelates with coordinatively unsaturated surface Fe-ions. They discuss literature data and outline that the increase of concentration of complexing agent change the activity towards iron dissolution from inhibitive to stimulative. Solubility of a complex is mainly determined by metal/ligand ratio, where 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 [23]. Moreover, these authors hypothesized that the chelating action could stabilize the Fe (II) ions of the passive film, giving a sparingly complex, much less soluble than the Fe (III) ions complex. 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 [23]. It was suggested that EDTA supported dissolution of the barrier layer and hindered formation of the outer barrier because its ability to chelate Fe (II) cations ejected from the oxide layer. Furthermore, EDTA adsorbs strongly in 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 Mole/L of EDTA enhanced generalised dissolution of steel [24].

The above results demonstrate that lactated ions have not 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 the pit propagation. When the calcium lactate is added to the test solution, the increase of calcium concentration causes the precipitation of a gel of calcium hydroxide. This gel deposited on the specimen surface forming a scale that incorporates lactate ions, as observed in the FTIR spectra. This scale could shield the specimen surface. The lactate ions does not contribute to the protectivity of the passive film, but they steric hindrance could reduce the contribution of the cathodic process and slow down the propagation of pit. This effect is not visible in the electrochemical tests, but becomes evident in long time exposure tests at the corrosion potential.

Fig. 5 shows that the inhibition of nitrite ions became evident when their concentration is comparable with hydroxyl ions concentration. The inhibiting properties of nitrites are discussed in several literature works [25-27] as a function of the chloride ion concentration. They prevent pitting initiation by promoting more stable films and stimulating the re-passivation kinetic on the fresh surfaces created into the pit embryo [2,25,28,29]. Nitrite ions cooperate with hydroxyl ions to re-form the protective film, as discussed in [5,6], one nitrite and one hydroxyl ion are involved to counteract the chlorides. This effect is only effective during the nucleation period, before acidification caused by the occluded-cell mechanism is too severe. After initiation, they produce severe penetration of localised attack owing to their oxidizing character that contributes to the anodic process. Insufficient nitrite content with respect to chloride can produce more severe penetration of localised corrosion thus the necessity to maintain an elevate concentration of nitrite ions in solution to preserve the steel from localised corrosion is well known and represent the mainly problem in the use of this inhibitor in concrete.

5. Conclusions

The inhibition properties of aspartate and lactate ions were evaluated by potentiostatic multiple specimen test in simulating pore solutions. Critical content for localized corrosion initiation was estimated through tests with progressive increase of chloride additions.

The aspartate ions showed an inhibition effect in concentration of 0.1 M that enhanced the critical chloride content. The effect is comparable with nitrite ions, at same concentration, but it vanish with further increase of concentration to 0.5 M. This behavior has been related to a chelating mechanism.

The calcium lactate did not increase critical chloride concentration. However, the formation of a massive scale was observed on specimens immersed in the solutions containing such substance that could explain the reduction of corrosion propagation observed in a previous experimental study on concrete slabs.

The results confirm the effectiveness of nitrite ions on critical chloride content. Their action became clearly visible at concentrations comparable or higher than hydroxyl ions concentration.

Acknowledgments

This research project has been made possible thanks to funding from ITALY® PROJECT of University of Bergamo. We would like to express our very great appreciation to Professor Francesca Fontana for her help in IR spectra. A special thank to Matteo and Alessandro for their contribution to the experimental.

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