# **Evaluation of Organic Acids as Corrosion Inhibitors in Chlorides Contaminated Alkaline Solutions by means of Cyclic Voltammetry**

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## Introduction

Chlorides penetration is the main cause of severe damage of rebar on marine constructions and highway concrete structures located in cold areas, due to de-icing salts. In order to improve the durability, inhibitors have been proposed as cost effective solution for extending the service life both as prevention techniques, for enhancing corrosion resistance of rebar on new structures, and as rehabilitation methods in corrosion damaged structures. Despite the relatively large number of substances considered in many experimental researches, nitrite based admixtures added during the concrete mixing are the only commercial effective inhibitors, providing a sufficient amount is added, more than the expected chloride content. The positive experience gained through years of use of inhibitors in other fields of application justifies further researches on new substances that do not show the limitations of current inhibitors developed for the reinforced concrete structure, but maintain effectiveness at least comparable to nitrites. Anions of organic acids are known as generalized corrosion inhibitors for carbon steel. Effects of inhibition of the pitting growth by means of long carbon chain organic acid salts were observed in buffered chloride containing solutions at pH 8.5 [1-5]. Inhibition behavior of different mono and polycarbossilic organic acid salts in alkaline chloride solutions were analyzed in a previous work by means of cyclic voltammetry technique [6]. This technique was considered by several authors for studying the localized corrosion of steel both in alkaline solution [5, 8-11] and in concrete [12-13]. This work studies the inhibition efficiency of sodium lactate and aspartate on chloride corrosion on steel rebar by means of cyclic voltammetry tests, compared with nitrite ions.

### **Experimental**

The tests were carried out in ASTM G5-82 standard cell, on disk specimens with 0.785 cm<sup>2</sup> exposed area. All specimens were grounded with emery paper (1200 SiC) and cleaned in acetone, than passivated in the alkaline test solution without chlorides for 72 hours. Rotating electrode at 2550 rpm rate was used in order to reduce diffusion effects. The tests had 60 s conditioning time at -1 V, followed by 15 s stabilisation at free corrosion potential. Afterwards, two cycles were run from -1.7 V to +0.7 V vs SCE at 50 mV/s scan rate. The test solution consisted of calcium hydroxide saturate solutions added with sodium hydroxide in order to increase the pH in the range from 12.6 to 14. Some tests without inhibitor were executed in solution with sodium and potassium hydroxide and in solutions without calcium, but no relevant differences were observed at constant pH. Sodium lactate and sodium aspartate were added to 1 M and 0.1 M concentrations, respectively. The comparison was done with 0.01, 0.1 and 1 M of sodium nitrite. Voltammetry tests were executed in the alkaline solution without any addition of chlorides, and with chloride concentration from 0.01M to 5M.

### **Results and Discussion**

Figure 1 shows the cyclic voltammetry curves of carbon steel in  $Ca(OH)_2$  saturated solutions, at pH 12.8. They show differ peaks that can attributed according to the electrochemical mechanism of iron dissolution in sodium hydroxide or calcium hydroxide described by R.S. Schrebler Guzmán et al and J.T. Hinatsu et al. [13-14], to the first oxidation of iron to Fe(OH)<sub>2</sub>, ferrous-ferric transformations in a hydrous outer oxide layer, and in a relatively

compact anhydrous inner oxide layer. At very high potentials, above  $E_{ox}$ , the current density increases owing to the oxygen discharge, which occurs 400 mV more anodic than the reversible potential owing to the high overpotential of oxygen evolution on metal oxide [15].  $E_{ox}$  decreases with increasing of pH according to the Nernst law.



potential / V vs SCE Figure 1: Cyclic voltammetry curves during first cycle on carbon steel in alkaline solution without and with chlorides ions



Figure 2: Effect of pH and chlorides content on E<sub>1</sub><sup>1st</sup> potential in absence of inhibitors

In the presence of chloride ions, the current in the passive region and the amplitude of the peaks generally increase but systematic effects were not recognized. At high potentials, the initiation of localised corrosion produces a noticeable increase in the anodic current densities before  $E_{ox}$  is reached, above the potential  $E_11^{st}$ , which depends on pH and chloride concentration of the solution (Figure 2). To evaluate  $E_{ox}$  and  $E_11^{st}$  from the voltammetric curves, the potential corresponding at the minimum value of the anodic current in the passive range (from -0.5 to 0.5 V vs SCE) increased of 10% was considered. For low contents of chloride and pH values rather alkaline, i.e. little or no critical conditions for localized corrosion,  $E_11^{st}$  takes much less noble values of  $E_{ox}$ . Thus, the difference ( $\Delta E$ ) between  $E_{ox}$  and  $E_1^{1st}$  was assumed as a parameter for evaluating pitting tendency. This parameter is shown in Figure 3 as a function of [CI]/[OH] ratio. A unique distribution was observed for all the tests,

indicating the pitting initiation in the range of 0.5 to 1 of [CI]/[OH<sup>-</sup>] ratio. The results are in agreement with literature data [16-18]. In solution with sufficient addition of very inhibiting chemical substance, the  $E_1^{1st}$  potential increases up to reach the value observed in absence of chloride ions, with an effect similar to that produced by an increase of alkalinity. Hence, in Figure 3, the value of  $\Delta E$  was related to the ratio between the chloride ions and the sum of hydroxyl ions and inhibitor concentration corrected by means of an empirical factor f<sup>\*</sup>. Higher is f<sup>\*</sup> higher is the inhibitor efficiency. The empiric value of f<sup>\*</sup> for nitrite was 0.8, for aspartate ions was 0.7, whereas it was only 0.02 for the lactated.



Figure 3: Distribution of  $E_{ox}$  - $E_1^{1st}$  potentials as a function of the hydroxyl ions and inhibitors ions

#### Conclusions

Cyclic voltammetry was used for studying the efficiency of chemical substances proposed for inhibition of pitting corrosion in alkaline solutions, at different pH and chlorides concentration. An empirical factor f\* was proposed to quantify the inhibitor efficiency. The highest value of f\* was obtained for nitrite. The inhibition effect of 0.1 M aspartate was similar to that of nitrite with the same concentration whereas lactate ions were much less effective.

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