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# Efficiency of an amine-ester based corrosion inhibitor for concrete

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This project discusses the behavior of a corrosion inhibitor, a water-based mixture of amines and esters, principally butyl oleate plus amines, for steel in concrete at three different dosages. Each dosage was evaluated in a concrete mix with a water/cement ratio of 0.6. The slabs included Portland cement concrete without inhibitor as the control. Non destructive test of steel reinforced concrete laboratory specimens were used. Specimens containing the manufacture's recommended dosage (100%) produced significant improvements in corrosion protection compared with the control, the 50% and 125% specimens. However after 400 days all the slabs showed more negative potential values than -350 mV (CSE) meaning a 90% corrosion probability. In general there is a good agreement in the inferences on the corrosion behavior made from each test performed.

*Keywords:* Corrosion; Concrete; Inhibiting admixtures dosage

## 1. Introduction

Reinforced concrete is a material widely used because it provides durability and strength. However, concrete structures exposed to marine environments deteriorate in a relative short period. Several corrosion protection systems have been developed to try to mitigate the corrosion problems. The corrosion-inhibiting admixture is probably the most cost-effective solution [1]. Even though corrosion inhibitors have been widely used over the years, there is still a debate regarding to long term benefits in order to extend the life of marine structures [2]. There is a rejection to use concrete corrosion inhibitors because they can't be changed if they result non effective, they can't be replenished if consumed, or they can't be removed if they have deleterious effects.

In general, corrosion inhibitors are classified on the basis of their mechanism of protection: anodic reaction, cathodic reaction or, in some cases, both (mixed). Mixed inhibitors are mainly used as a preventive measure for new structures and are designed to retard the corrosion onset [3]. Additionally, a system of concrete corrosion prevention would protect the reinforced steel from the beginning of corrosion during the life of the structure.

The main advantages of the inhibitors are:

1. The admixture is uniformly distributed throughout the concrete; therefore all of the steel is equally protected.
2. The use of admixtures is not skill dependent; it only consists of adding the correct amount of admixture.
3. Construction quality control generally is not concerned with admixtures as it is with other methods (i.e. epoxy coatings) [4].

The Inhibitor tested, a water-based mixture of amines and esters, principally butyl oleate plus amines, act to form a protective organic layer on the rebars (chelating process). This inhibitor is classified as passive-active, meaning that

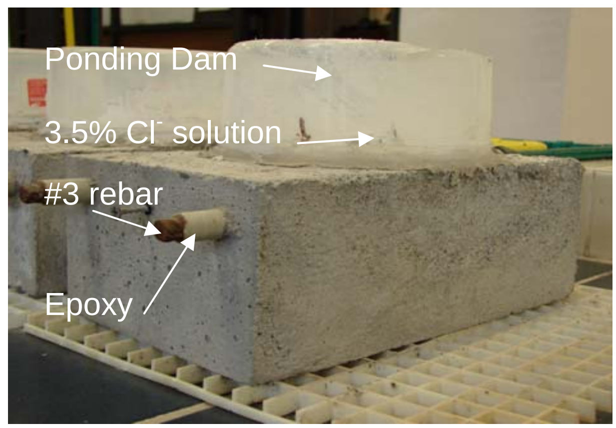


**Figure 1.** Geometric design of the Concrete slabs used during the experimentation.

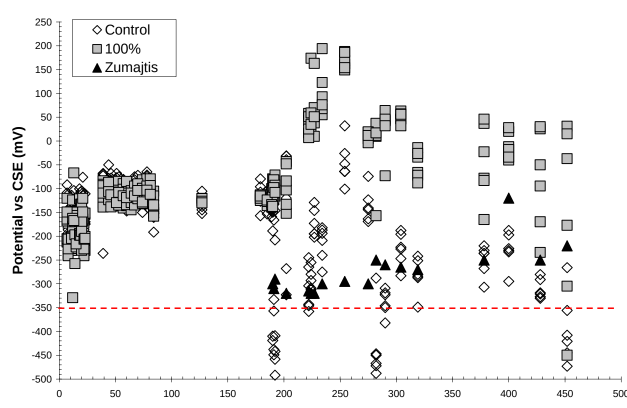


**Figure 2.** Plot of the free corroding potential data for the Control, the 100% slabs and the Zumajtis slabs.



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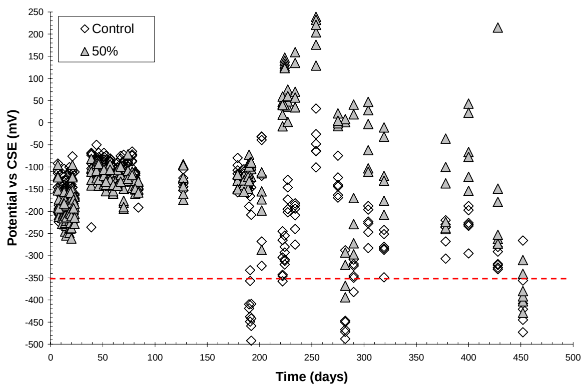


**Figure 3.** Plot of the free corroding potential data for the Control and the 50% slabs.

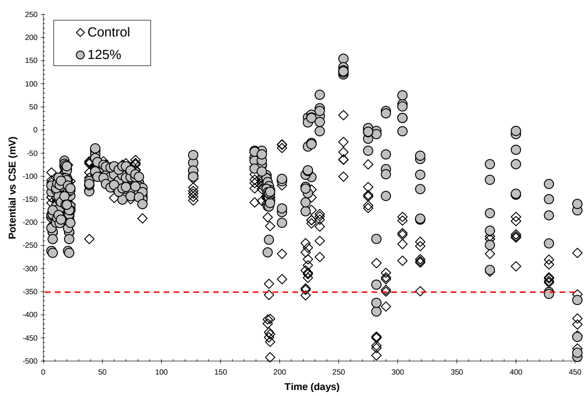


**Figure 4.** Plot of the free corroding potential data for the Control and the 125% slabs.

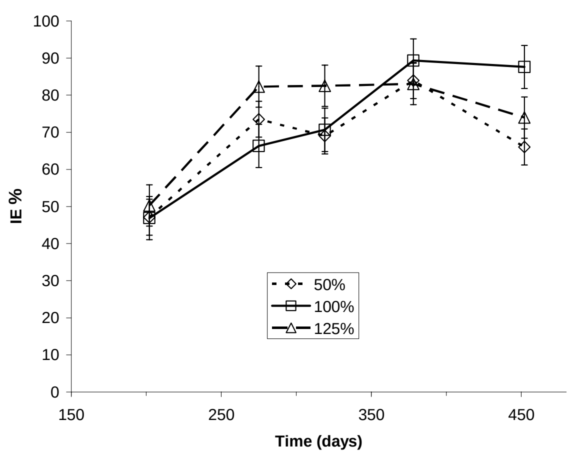


**Figure 5.** Inhibitor Efficiency data for the three dosage used.

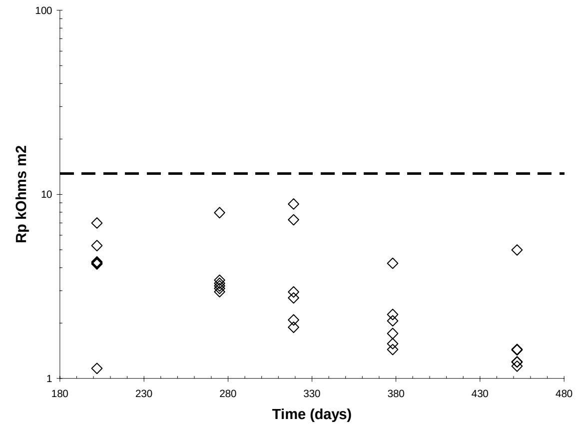


**Figure 6.** Polarization resistance of the Control Slabs.

in addition to mitigation iron dissolution, it also reduces the ingress of chloride ions into concrete by lining the pores in concrete with a compound (calcium salt) that makes the concrete hydrophobic. Inhibition of anodic and cathodic reactions is done by an organic film formation adsorbed to the reinforcement surface which acts as a physical barrier slowing down the electrochemical reactions of the corrosion process. This type of inhibitor would inhibit both, the anodic and cathodic reaction (mixed type) [5].

Several corrosion inhibitors have been used for the last 20 years on new or rehabilitated concrete bridges to extend their service lives. The most common ones are active inhibitors based on inorganic nitrites. Some authors had compared the efficiency of several inhibitors [6-9] including the one of this project: Troconis and Perez [6] tested several inhibitors (Triethanolamine, Sodium

Molibdate, Lead Hydroxide, Calcium Nitrate, Lead Nitrate, Calcium Phosphate, Lead Oxide, Sodium Nitrite, Basic Calcic Phosphate, Zinc Oxide, and Calcium Nitrite). They found that a mix of 2% Zinc Oxide and 2% Calcium nitrite had the best corrosion inhibiting behavior. Yunovich and Thompson [7] made a literature review of inhibiting admixtures including the one of this project, and they concluded that there is a need for a comprehensive testing program so the results obtained could be used to model a predictive useful life of a structure. Cuccson, Qian, Chagnon and Baldock [8] made an assessment of the field performance of nine corrosion-inhibiting systems applied on a major highway bridge in Canada (Epoxy-coated reinforcement Rebar, Concrete coating-polymer-based liquid blend, Alkanolamines, Organic-inorganic concrete admixture-amine derivatives, Sodium nitrite, Rebar coating water-based epoxy, Organic Amines and esters, Organic Alkanolamines and Amines, Organic alkanolamines, ethanolamine, and phosphate, and calcium nitrite) they concluded that Calcium nitride, consistently provided good

performance in all the corrosion measurements. Y. Xi, N. Abu-Hejleh, A. Asiz & A. Suwito [9] from the Colorado Department of Transport (CDOT), made an evaluation of different corrosion control systems, among them: High Performance Concrete, Alternative reinforcement and corrosion Inhibiting Admixtures. Three major

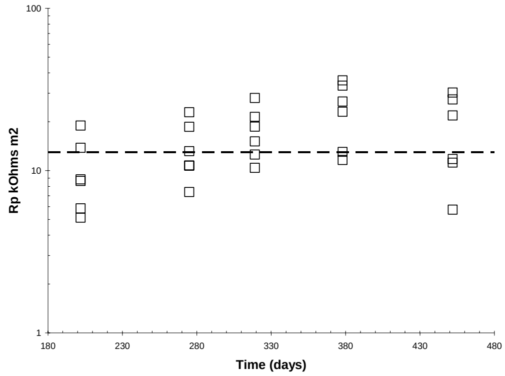


**Figure 7.** Polarization resistance of the 100% Slabs.

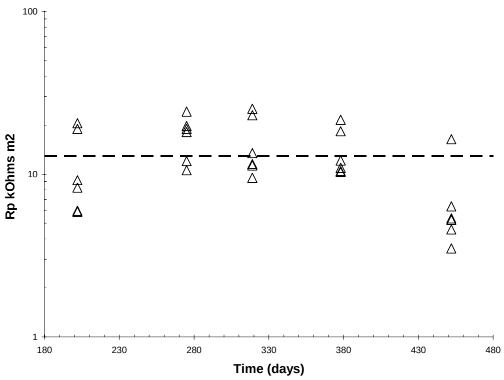


**Figure 8**. Polarization resistance of the 50% Slabs.

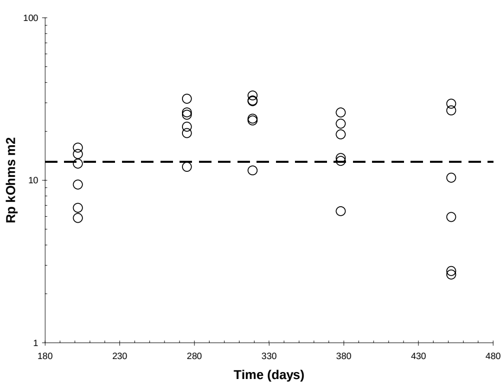


**Figure 9.** Polarization resistance of the 125% Slabs.

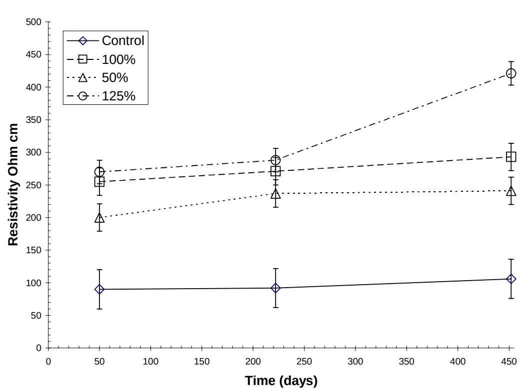


**Figure 10.** Solution Resistivity of all the slabs as a function of time.

commercially available corrosion inhibitors are described in detail, one produced by W.R. Grace and Co., one by Master Builders, and the last one by Sika Corporation. They made some recommendations, however the CDOT engineers do not use these recommendations because of a lack of a method to predict the chloride level at the surface of steel rebars. Additionally, CDOT has no specific policy for the use of corrosion inhibitors.

Since most of the commercially available inhibitors blends contain several active components, it is probable that more than one inhibition mechanism is operating in order to suppress corrosion. However, due to the commercial sensitivity of the inhibitors formulation, much of the manufacture's published literature lacks quantitative data concerning the concentration of inhibitor required to be adsorbed in order to bring about an effective level of inhibition. The purpose of the project is to evaluate the effect of the dosage of a water-based mixture of amines and esters corrosion inhibitor on the onset and the progression of corrosion in concrete.

## 2. Experimental

Twelve concrete slabs of 15 x 10 x 25 cm with a water/cement ratio (w/c) of 0.60 and two 0.95 cm (3/8") rebars embedded in the concrete in each slab were cast (Figure 1).

Three slabs were used without any inhibitor as Control samples, three slabs of each of the three different concentrations (50, 100 and 125% of the recommended dosage (5 $kg/m^3$ =100%) were used. Each rebar was numbered according to the following code:

Control Group (without Inhibitor) → 3 probes (rebar 1 to 6)

100% Inhibitor Group → 3 probes (rebar 7 to12)

50% Inhibitor Group → 3 probes (rebar 13 to 18)

125% Inhibitor Group → 3 probes (rebar 19 to 24)

After a 28 days curing period, the slabs were set in a controlled Relative Humidity (RH) environment and the electrochemical variables monitoring started. After a period of 192 days under controlled environment, the slabs were set at laboratory environment (average 25°C and 63 % RH) and a ponding system was used to expose the concrete slabs to wet/dry cycles using sodium chloride solution (3.5% cement weight). All the specimens had a seven day ponding period followed by a twenty one day drying period, for a total cycle length of 28 days. Slabs specimens were dried at room temperature during the drying periods.

Six porosity specimens, 5 X 5 X 5 cm, were cast concurrently, in the same manner and at the same time that the corrosion specimens. After 60 days, specimens were tested for porosity.

The following measurements were made on each of the slabs at regular intervals:

Linear Polarization Resistance (LPR); Open circuit potentials (mV copper sulfate electrode [CSE]); Solution resistance between rebar mats (ohms); and Porosity Tests.

## 3. Results y Discussion

Figure 2 shows a plot of the evolution of the free corroding potential data for the Control and the 100% slabs. Measurements more negative than the threshold value, –0.35V (CSE) (dotted line) indicates a 90 percent probability that corrosion is occurring in the rebar. The 100% Slabs had values less negative than –0.35V (CSE), indicating no corrosion. The Control slabs since day 280, had values more negative than –0.35V (CSE), indicating a 90% corrosion probability.

The values shown at days 192, 282 and 452, were the beginning of the wet cycles, as it can be observed by the lower potential values due to the lowest resistivity of the concrete. The same behavior could be observed at the three inhibitor dosages used.

Zemajtis [10] using the same inhibitor used in this research (Figure 2), found that at the beginning of the test, the potentials were at the level of uncertain probability of corrosion, and at the end of their experimentation, the potentials were slightly lower, suggesting lower corrosion damage. Even though the testing conditions of the present experimentation were different from the Zemajtis ones (the NaCl solution was at 6% by weight), the results seem similar regarding the behavior tendency towards more positive potential values suggesting possibility of no corrosion activity.

Figure 3 shows a plot of the free corroding potential data for the Control and the 50% slabs. Although the 50% slabs had values slightly less negative than the Control slabs, there were not clear differences between them. At day 280, both showed the same tendency towards more negative potentials even though the potentials for the 50% slabs were slightly more positive.

Figure 4 shows a plot of the free corroding potential data for the Control and the 125% slabs. Although the 125% slabs had values less negative than the Control slabs, in general the tendency of the Control slabs was toward more negative values and the 125% slabs had a tendency towards more positive values.

The polarization resistance, Rp, is the slope of the plot potential vs current. The corrosion rate can then be determined through the Stern-Geary equation (1). The lowest the Rp value, yields the highest corrosion rate.

$$I_{corr} = \frac{B}{R_p} \tag{1}$$

Where:

$R_p$ = *plarization resistance*

$i_{corr}$ = *corrosion current*

$B$ = *proportionality constant*

The Rp was used to calculate an *Inhibitor Efficiency (IE)* as follows:

$$\%IE = \frac{R_{p(inhib)} - R_{p(without\ inhib)}}{R_{p(without\ inhib)}} * 100 \tag{2}$$

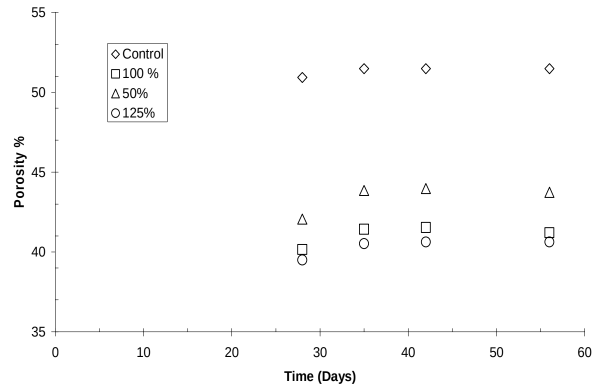


**Figure 11.** Porosity of the slabs as a function of time.

Figure 5 shows the Inhibitor Efficiency as a function of inhibitor dosage applied. As it can be seen, the 100% inhibitor dosage was the most effective inhibiting corrosion, in average around 17% more effective than the 125% dosage and around 26% more than the 50% dosage.

Figure 6 shows the Polarization Resistance (Rp) for the Control Slabs. Rp values were in the range 0–10 kOhms m$^2$, thus implying a high corrosion rate according to the Stern Geary Equation. The dotted line shows the threshold value for the corrosion initiation (B= 0.026 V and I=0.2 µA/cm$^2$ from the Stern-Geary equation.)

Figure 7 shows the polarization resistance plot for the 100% slabs, the values oscillated around 20 kOhms m$^2$, implying a large improvement, around four-fold, on the corrosion rate according to the Control slabs at the largest value reached.

Figure 8 shows the polarization resistance plot for the 50% slabs, the values oscillated around 10 kOhms m$^2$, however, towards the end of the testing period, a three-fold decrease of the lowest Rp is shown, implying an increase on the corrosion rate.

The Figure 9 presents the polarization resistance for the 125% slabs. The average Rp was slightly higher than the 100% slabs; however it also showed the maximum data dispersion varying from 33 to 1 kOhms m$^2$.

The Figure 10 presents the solution resistivity of all the slabs as a function of time. The resistivity for the control slabs was around 100 Ohms during the testing period. The 100% slabs had only a slight increase in resistivity from 200 to 241 ohms cm. There was a sharp rise from the beginning for the 125% slabs from 250 to 421 ohms cm. The 50% slabs kept a value around 220 ohms cm during the testing period. The resistivity of the solution for the 125% slabs was at least a three-fold increase in resistivity over the one of the Control slabs and a two-fold for the 100% slabs.

The porosity was calculated with the following equation [11]:

$$\%Porosity = \frac{W_h - W_d}{W_h - W h'} * 100 \tag{3}$$

Where:

*Wh = mass of saturated, surface dry (g)*
*Wd = mass of oven dry (105°C) (g)*
*Wh' = buoyant mass of specimen (g)*

Figure 11 presents the porosity results. As expected, the porosity was larger for the Control slabs and the lowest porosity corresponds to the 125% slabs, this is believed to be due to the protection mechanism that lining the pores in concrete with a calcium salt that makes the concrete hydrophobic.

## 4. Conclusions

The Inhibitor tested at 100% dosage produced significant improvements in corrosion protection compared with the control concrete and with the other two different dosages.
After 15 months of corrosion monitoring, specimens with 100% recommended dosage seemed like they just started to show signs of corrosion.

The 50% slabs around day 180 lost their passivity showing clear signs of corrosion.

The125% slabs had a similar behavior to the 50% slabs; however, the open circuit potential did not reached values so positive like the 50% slabs.

All three dosages of the corrosion inhibitor delayed the onset of corrosion up to certain degree.

The results from the electrochemical tests used (Open circuit potential, Polarization resistance, porosity and solution resistance) were in agreement.

After 15 months of testing, control slabs were actively corroding, this has started after 280 days. From this, it was evident that a considerable amount of time was needed in order to obtain any result from this type of test.

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