

## Passivating action of an organic inhibitor on the steel of reinforced concrete

E. Anzola\*, R. Malavé\*, V. Barrios\*, D. Villarroel\*, A. Tiso\* and M. Parra\*

**Abstract** An electrochemical evaluation has been made on a concrete mix with an organic inhibitor added, in order to establish its contribution to the formation of a protective film on the steel surface. Concrete cylinders (6" × 3"), each with a 3/8" steel bar and two graphite electrodes embedded, with two water/cement ratios (0.40 and 0.55) were used as testing samples. Reinforced steel bars, both chemically cleaned and in the as rolled condition, embedded in salted and unsalted concrete mixes, were used to test if chemical adsorption occurs in each condition. Samples were soaked into brine solution during 365 days as to simulate a sea environment. During exposure period readings of potential, corrosion rate and potentiodynamical cyclic curves were made. It can be concluded that the organic inhibitor needs a low water/cement ratio mix (0.40) in order to react via a chemical adsorption on the steel, being more effective on cleaned surfaces.

**Keywords** Concrete. Inhibitor. Corrosion. Admixtures.

### Evaluación de la acción pasivadora de un inhibidor orgánico sobre el acero del concreto armado

**Resumen** El objetivo del trabajo es hacer una evaluación electroquímica para inferir sobre la formación de la película pasivante en la superficie del acero, por parte de un inhibidor orgánico adicionado a la mezcla de concreto. Para esto se elaboraron probetas de concreto armado de 3 × 6 pulgadas con acero de refuerzo de 3/8 pulgadas de diámetro y dos electrodos de grafito en su interior, usando mezclas de relación agua/cemento 0,40 y 0,55; con y sin sal. Se utilizó acero limpiado por medios químicos y también en condiciones normales de uso. Las probetas se colocaron en agua salada durante 365 d, realizándose mediciones de potencial, velocidad de corrosión y curvas cíclicas potenciodinámicas. Se puede decir que el inhibidor actúa solo para relaciones agua/cemento de 0,40, observándose mejores resultados en las probetas con acero limpiado, indicando que el estado superficial del acero influye en la reacción de quimiadsorción del inhibidor.

**Palabras clave** Concreto. Inhibidor. Corrosión. Aditivo.

## 1. INTRODUCTION

Nowadays, the use of reinforced concrete is more extensive than that of any other material, thus the understanding of endurance of reinforced concrete structures becomes a very important issue. The damages caused by corrosion are not evident until critical failure levels are reached, making repairs of corroded structures complex and expensive. Therefore corrosion should be prevented right from the design stage of structures.

When chloride ions enter the concrete mix, the attack that occurs is due to exposure of the reinforced concrete steel to a seawater or misty environment, present in coastal zones. Venezuela is

a country with an extensive coastline and a high proportion of its buildings such as oil refineries, shipping docks, resort areas and so on, are exposed to marine environments. Structures exposed to such an environment demand a high quality concrete mix, with great resistance, high density, waterproofing and low porosity. These requirements can only be met by low water/cement ratios, rich cement mixes and thick concrete layers around the steel frames<sup>[1]</sup>. Further steps are to be considered in order to avoid corrosion under very hostile environmental conditions.

The use of concrete with inhibiting admixtures is a safe alternative requiring low investments to control corrosion of steel bars, which in turn

(\*) Universidad Centroccidental "Lisandro Alvarado" – Decanato de Ingeniería Civil, Barquisimeto-Venezuela.

produces significant advantages compared to other protecting systems. Among those are organic corrosion inhibitors (OCI), recently introduced in the market. They are a water-based blend of esters and amines, which are added to the concrete mix as any other liquid admixture. Its main advantage is given by a chemical adsorption reaction mechanism which creates a protective film on the steel surface. This protection is independent of the concentration of the chloride ions, because its reaction mechanism does not compete with these ions<sup>[2]</sup>.

The action of this additive has been studied since 1995<sup>[3 and 4]</sup>, and its capacity to form a protective film on steel surfaces, which are not thoroughly cleaned, is still doubtful<sup>[5]</sup>. Therefore the aim of the present work is the electrochemical evaluation of concrete mixes with an organic corrosion inhibitor (OCI) admixture in order to establish its contribution to the formation of a passive film on both unclean and clean steel surfaces.

## 2. EXPERIMENTAL PROCEDURE

Electrochemical evaluation tests were conducted on reinforced concrete samples with an OCI admixture added, in order to measure potentiality, corrosion rates and potentiodynamical cyclical curves.

Ideally the formation of a passive film on the steel surface should be seen through a Scanning Electron Microscope (SEM). However in this case the use of such a technique is very limited as the steel is fully embedded in the concrete. Furthermore any attempt to remove the steel from the sample by impact will destroy the film.

Some researchers<sup>[6]</sup> have observed, through X-

Ray Photoelectron Spectroscopy (XPS) and Auger Electro Spectroscopy (AES) and using several chemical substances, the formation of passive film on bare steel samples cleaned chemically.

### 2.1. Materials selection and samples construction

Concrete samples were produced using local washed sand and crushed stones (1/2" nominal size), type 1 Portland cement, municipal running water and a commercial organic corrosion inhibitor (OCI) admixture which is a water-based chemical blend of esters and amines. Its reaction mechanism is based on a chemical adsorption on the steel surface which creates a protective film. Two water/cement ratios (0.40 and 0.55) and both salted (3.5 % cement weight), to speed-up the corrosion process, and unsalted concrete mixes were used in the samples. Reinforcing steel bars, chemically cleaned and in the as rolled condition were used in each case.

Concrete cylinders (6"×3"), each with a 3/8" steel bar and two graphite electrodes (a reference one and an auxiliary), were used as testing samples, as specified by the Corrosion Centre of *La Universidad del Zulia LUZ*<sup>[7]</sup> (University of Zulia, Maracaibo-Venezuela).

80 samples were made in total, as shown in table I, half of them used a 0.40 water/cement ratio and a 0.55 ratio for the other half. Each of these groups, in turn, was split into 20 salted samples (CS) and 20 unsalted samples (SS). Finally 50 % of the latter used reinforcing steel bars chemically cleaned (L) while the remaining 50 % used steel in the as rolled condition (SL).

All samples, once settled, underwent a 28 days curing period before being soaked into a 3.5 %

Table I. Sample arrangement

Tabla I. Preparación de las muestras

Group sample	Designation	Number of samples	Water/cement ratio	Water mix	Steel surface condition
1	SS-SL-0.40	10	0.40	No salt added	As rolled conditions
2	SS-L-0.40	10	0.40	No salt added	Pre-cleaning treatment
3	CS-SL-0.40	10	0.40	3.5% by weight	As rolled conditions
4	CS-L-0.40	10	0.40	3.5% by weight	Pre-cleaning treatment
5	SS-SL-0.55	10	0.55	No salt added	As rolled conditions
6	SS-L-0.55	10	0.55	No salt added	Pre-cleaning treatment
7	CS-SL-0.55	10	0.55	3.5% by weight	As rolled conditions
8	CS-L-0.55	10	0.55	3.5% by weight	Pre-cleaning treatment

brine solution. Samples were submitted to 2 h dipping - 22 h aeration cycles during 365 days.

## 2.2. Electro chemical evaluation

The evaluation was conducted during the exposure period to measure potential, corrosion rates and potentiodynamical cycles curves.

### 2.2.1. Potential measurements

These were made every 5 days using a digital multimeter with Cu/CuSO<sub>4</sub> saturated electrodes, according to ASTM C876-87 specifications.

### 2.2.2. Corrosion rate

Measurements were made using a 263 A potentiostat via a polarization resistance technique, which measure the apparent resistance of a testing cell when an electrode is polarized between 10 and -20 mV<sup>[8]</sup>. This test was done every 15 days.

### 2.2.3. Cycling polarization and potentiodynamical curves

These tests were made with a 263 A potentiostat which acted on the formation of the passive film as means to figure out the corrosion process occurring on the steel embedded in the concrete. The technique is based on the transfer of a potential applied from the cathodic zone to the anodic one at a speed slow enough, in both directions, (0.28 mV/sec.) to allows the formation of a protective film.

## 3. ANALYSIS AND TEST RESULTS

Results are given for salted samples tested only during 90 days, as the effects were already apparent after such a period, while the set of unsalted samples was evaluated during 365 days.

### 3.1. Potential measurements

As shown in figure 1 unsalted samples (SS) have passivity potential values close to -150 mV in all cases, including the clean steel samples (L) and the unclean ones (SL). According to the ASTM C876-87 Standard<sup>[9]</sup>, potential values between -200 mV and -100 mV indicate that there is a 10 % probability for corrosion to occur on the reinforcing steel.

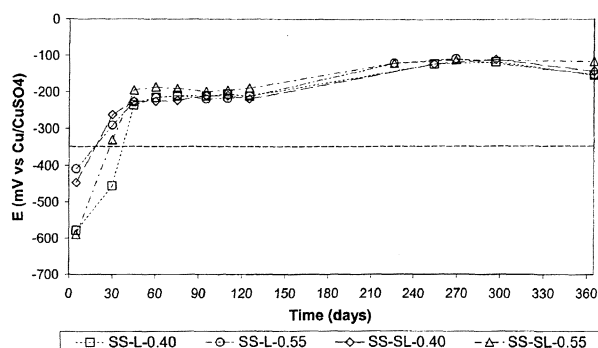


Figure 1. Potential measurements for non salted mixtures (SS).

Figura 1. Medidas de potencial para las muestras sin sal (SS).

On the other hand figure 2 shows, using salted samples (CS) with a 0.55 water/cement ratio, potential measurement readings below -350 mV, indicating that there is a 90 % probability for corrosion to occur on the reinforcing steel<sup>[9]</sup>. Potential measurements readings of -300mV and -250mV at 90 days on the 0.40 ratio samples (CS) for unclean and clean steel were obtained respectively, which indicates a 50 % probability for corrosion to occur on the steel surface<sup>[9]</sup>.

Apparently samples with a 0.40 water/cement ratio, either for clean or unclean steel, perform better than those with higher ratios (0.55) as the latter display more negative potentials. Best performance is only obtained when using a clean steel surface.

### 3.2. Corrosion rate

As shown in figure 3, for unsalted samples corrosion rate values are below 0.1  $\mu\text{A}/\text{cm}^2$  for a 0.40 water/cement ratio, while samples with a 0.55 ratio reached higher corrosion rates; corrosion rate values falling within 0.1 to 0.2  $\mu\text{A}/\text{cm}^2$  are

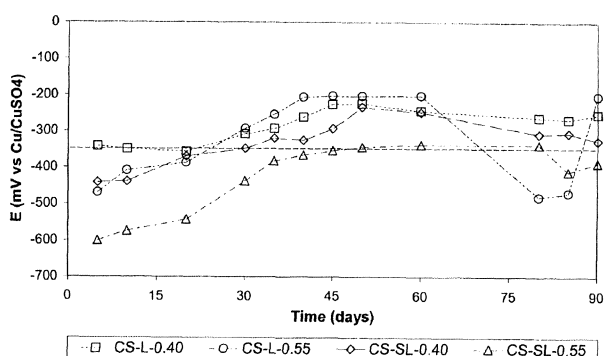
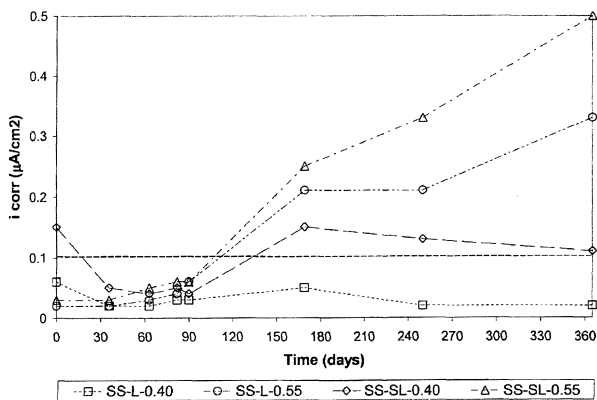


Figure 2. Potential measurements for salted mixtures (CS).

Figura 2. Medidas de potencial para las muestras con sal (CS).



**Figure 3.** Corrosion rate measurements for non salted mixtures (SS).

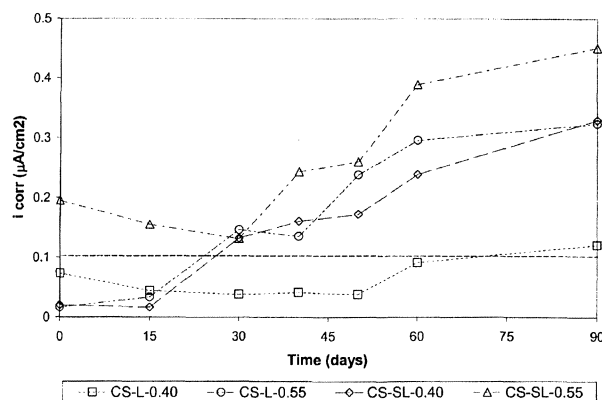
Figura 3. Medidas de velocidad de corrosión para las muestras sin sal (SS).

negligible<sup>[10]</sup>. Therefore the sample results indicate that the metal surface condition contributes to the formation of a passive film on the steel surface due to the action of an organic corrosion inhibiting admixture (OCI).

Figure 4 shows, using salted samples with a 0.55 water/cement ratio in both cleaned and non cleaned steel surfaces, very high corrosion rate values observing chlorides attack to the reinforcing steel; while using a 0.40 ratio and a clean steel better results were reached, which indicates that the inhibitor reacted more effectively.

### 3.3. Potentiodynamical cycling polarization curves

These curves were drawn either after a 28 days curing period or before beginning the exposure



**Figure 4.** Corrosion rate measurements for salted mixtures (CS).

Figura 4. Medidas de velocidad de corrosión para las muestras con sal (CS).

period to the salty solution and at the end of the total exposure time.

Figure 5 shows a typical curve; the results reached, prior to and after the exposure time to the salty environment, by the unsalted mixtures for both ratios (0.40 and 0.55) and using clean and unclean steel were similar in all cases. It can be seen on the curve (Fig. 5) that the reverse current goes towards positive potentials, this could mean that a passive film was formed irrespective of the steel surface condition. However for 0.55 ratio samples the return section of the curve moves towards values closer to corrosion potentials.

Figure 6 shows a typical curve for salted samples after 28 days of curing. As can be seen, the values of the current registered on the reverse side of the curve move towards negative potentials, indicating that the passive film was not created as the presence of chloride ions interfered with the passive film formation.

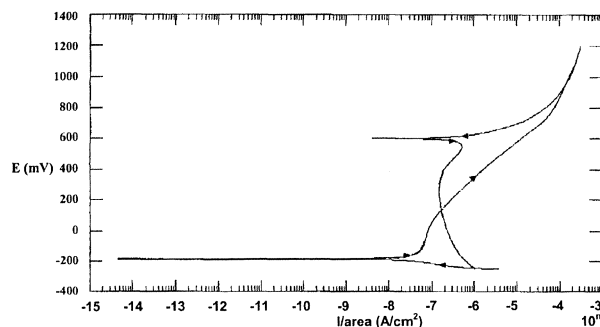
## 4. CONCLUSIONS

It can be concluded that the organic corrosion inhibitor (OCI) admixture needs a low water/cement ratio mix (0.40) in order to react via a chemical adsorption on the steel, being more effective for cleaned surfaces.

According to cycling polarization curves, the presence of chloride ions in the mix does not allow the formation of a passive film, leaving the steel surface unprotected.

## Acknowledgements

We would like to thank the Universidad Centroccidental "Lisandro Alvarado" UCLA (Central Western University "Lisandro Alvarado,



**Figure 5.** Typical potentiodynamic cyclic curves, for non salted mixtures (SS).

Figura 5. Curvas cíclicas potenciodinámicas típicas de las mezclas sin sal (SS).

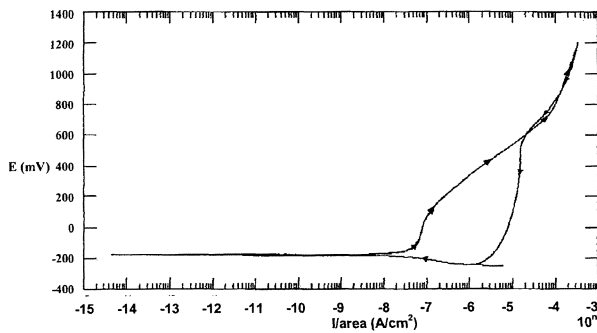


Figure 6. Typical potentiodynamic cyclic curves, for salted mixture (CS).

Figura 6. Curvas cíclicas potenciodinámicas típicas de las mezclas con sal (CS).

Barquisimeto-Venezuela) for the support given to the this work through the Consejo de Desarrollo Científico, Humanístico y Tecnológico CDCHT (Council for Scientific, Human and Technological Development UCLA, Barquisimeto-Venezuela) and the UCLA-DIC Materials' Laboratory.

## REFERENCES

- [1] V. O'REILLY, *Rehabilitation of corrosion Damaged Infrastructure*. NACE International, 1998, pp.
- [2] C. NMAI, *Concr. International* 14 4 (1992) 45-54.
- [3] E. ANZOLA, R. MALAVÉ and J. ARROYO, *Rehabilitation of corrosion Damaged Infrastructure*, NACE International, 1998, pp. 153-167.
- [4] E. ANZOLA, J. HERRERA, R. MALAVÉ and R. SUÁREZ, *Memorias V Congreso Iberoamericano de Patología de las Construcciones y VII de Control de Calidad*, Montevideo, Uruguay, 1999.
- [5] O. RINCÓN and O. PÉREZ, *Rehabilitation of corrosion Damaged Infrastructure*. NACE International, 1998.
- [6] J.L. FANG, Y. LI, X.R. YE, Z.W. WANG and Q. LIU, *Corrosion* 49 4 (1993) 266-271.
- [7] O. PÉREZ, O. MORÓN, O. GARCÍA y O. RINCÓN. *Memorias del I Congreso de Corrosión NACE-Región Latinoamericana y I Congreso Venezolano de Corrosión*, Maracaibo (Venezuela), Publicación N°. 94104, 1994.
- [8] O. TROCÓNIS and M. SÁNCHEZ. *I Simposio sobre estructuras de concreto armado, control de la corrosión y rehabilitación*, 1992.
- [9] ASTM C 876-87.
- [10] C. ANDRADE, *Manual de Inspección de Obras Dañadas por Corrosión de Armaduras*, 1ª Ed., Instituto Eduardo Torroja, Madrid (España), 1998, pp. 85-87.