Impact of the corrosion inhibitors in the durability of concrete structures

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Abstract*–The phenomenon of chloride corrosion represents one of the most significant deterioration processes in reinforced concrete structures located mainly in marine environments. The effects of corrosion can mean high maintenance and repair costs. Therefore, the need arises to use mechanisms that mitigate the consequences of corrosion such as corrosion inhibitors and thus extend the useful life of structures. Aim of the present paper is to analyze the economic impact of the use of corrosion inhibitor additives on the durability of reinforced concrete structures. To achieve this, a life cycle cost analysis of different case studies with and without corrosion inhibitors was performed using software. Obtaining a higher cost-benefit ratio throughout the useful life of the structures with corrosion inhibitors for each case study, especially those that have a water / cement ratio lower than 0.5 where greater efficiency of the inhibitors is evidenced.

Keywords—corrosion, additives, reinforced concrete structures

I. INTRODUCTION

One of the great challenges that construction professionals have had to face to this day is to guarantee the durability of reinforced concrete structures and this is due to the reason that on certain occasions during the conception of their design and execution the environmental and climatological conditions to which they will be exposed are not taken into consideration.

For this reason, designers, and builders to ensure a reinforced concrete structure lasts for years until it reaches the maximum of its desired useful life, must propose strategies capable of contemplating all possible degradation factors and elaborate based on them, the pertinent actions to counteract them in each of the phases of the project construction and use of the structure [1].

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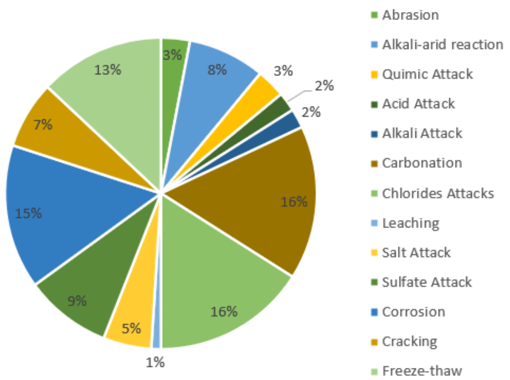

Fig. 1 Physical and chemical mechanisms of concrete deterioration [2].

As can been observed in Figure 1, the factor that has the greatest incidence in the degradation of reinforced concrete structures is the phenomenon of corrosion. Its high degree of affectation in the deterioration of the reinforcements, and therefore of the structure, lies in the loss of adhesion between the concrete and the steel, in the decrease of the resistance product of the reduction of the cross-section of the reinforcement rods and, in the cracking of the concrete mass because of an increase in the volume of steel product of all the rust generated by the corrosion.

These effects would result in a significant reduction in the life cycle of the structure as the level of corrosion continues to increase, which will depend on the exposure conditions to which the structure is located and could have a detrimental effect on repair and maintenance costs over the life of the structure [3].

From the economic point of view, it is estimated that the annual cost of corrosion worldwide exceeds 1.8 trillion dollars, which translates into 3-4% of the Gross Domestic Product (GDP) of industrialized countries [4]. Reference [5] suggest that the cost of rehabilitating corrosion-affected CR structures now accounts for 50% of total construction expenditure. Even in the UK, it was estimated that spending on concrete repair far exceeded one billion pounds sterling in 2003 [6].

These are some of the many examples of the economic impact caused by corrosion on reinforced concrete structures and with which the great magnitude of this problem is evident. In this context, various studies and research have emerged to determine mechanisms and new materials that from the durability criteria allow to mitigate the damages caused by corrosion and increase the service time throughout the life cycle of the structure and thus not resort to high costs in repair and maintenance of the same.

Therefore, and to encourage the scientific community of Ecuador, considering that very little research related to the influence of corrosion on the durability of structures is presented, the present work aims to analyze the cost of the life cycle of the use of corrosion inhibitor additives in the durability of reinforced concrete structures.

II. STATE OF THE ART

2.1 Corrosion

Corrosion can be understood as the interaction between a metallic material and the environment that surrounds it, causing the deterioration of its physical and chemical properties. This phenomenon can develop through two different mechanisms, either by direct oxidation (dry corrosion) or by the intervention of an aqueous or electrochemical solution (wet corrosion) [7].

Dry corrosion occurs when in the absence of a liquid medium, a metal reacts with vapors and gases usually at high temperatures [8]. On the other hand, wet corrosion does require the participation of an aqueous solution and at the same time to exist an electric potential difference along with the metal in such a way that an electrochemical cell is established, whose composition is made up of four basic components: electrolyte, anode, cathode, and conductor [9].

The electrolyte is the current-carrying medium, which in the case of steel embedded in concrete, would be the water contained in the pores of the cementitious matrix. The anode (positive electrode) is in contact with the electrolyte and corrosion will occur through an oxidation reaction involving the formation of ions and the release of electrons [10]. The cathode (negative electrode) is also in contact with the electrolyte, but no corrosion occurs, so the metal remains unchanged [11]. Finally, the conductor connects the anode and cathode to complete the circuit and allow current flow.

Thanks to the high alkalinity (pH around 13) present in the pores of the concrete, a passive layer composed of iron oxides and hydroxides that gives protection to the steel is developed at the steel-concrete interface [12-13]. This passive layer slows the rate of corrosion to the point of rendering it null. Therefore, corrosion can only start once the layer is destroyed and the steel is unprotected [12].

The rupture of the passive layer is caused by the loss of the alkalinity of the concrete when it reacts with substances such as CO_2 (carbonation) or when it is exposed to the presence of chlorides.

When carbon dioxide penetrates concrete in the presence of moisture, a reaction occurs with the calcium hydroxide that composes the cement and forms calcium carbonate that eliminates the hydroxyl ions of the pore solution, with which the pH of the concrete is reduced to reach values less than 9, therefore the passive layer of the steel is disabled, and the corrosion process begins [14].

Carbonation deterioration happens more quickly when the reinforcing steel is not adequately coated. Or in turn, when the concrete is characterized by high porosity since the pores facilitate the diffusion of CO_2 inside the concrete mass. This would be caused mainly by a low cement content, a high water-cement ratio, and poor curing of concrete [15].

The exposure of reinforced concrete to chlorides is the main cause of premature corrosion in reinforcing steel since carbonation is not as common and is usually a process that takes longer to reduce the alkalinity of the concrete and thus corrode the reinforcing steel [16].

To continue the corrosion process, it is necessary that water is regenerated, and oxygen consumed. Therefore, there is no chloride corrosion in dry concrete, probably at a relative moisture of less than 60%. Just as corrosion cannot originate in concretes that are completely submerged in water. The optimal relative moisture for corrosion is 70 to 80%. At higher relative moistures, oxygen diffusion through concrete is significantly reduced [17].

Unlike carbonation, chloride attack causes corrosion to spread in localized ways, generating what is known as pitting corrosion. This happens when chloride ions enter the steel-concrete interface and reach a critical value on the surface of the steel. At that point, the onset of pitting corrosion is established, and it will be known to transcend only if moisture and oxygen are available [18]. Chloride-induced corrosion is one of the most common concrete deterioration processes in coastal environments, and on which this research focuses.

2.2 Corrosion inhibitors

Over the years, various technologies have been developed to combat the effects caused by corrosion in reinforced concrete structures. Among these, we can highlight coatings with epoxy paint, cathodic protection, stainless steels, galvanized, corrosion inhibiting additives, among others.

While it is true, numerous studies have been conducted to test the effectiveness of corrosion protection mechanisms, particularly, the use of corrosion inhibitors has been of enormous interest since past decades, given that they are claimed to be useful not only as a preventive measure for new concrete structures (as an addition to the mixture) but also as restoration techniques to protect existing structures that already show signs of corrosion attacks.

According to [19], a corrosion inhibitor additive can be defined as a chemical that decreases the rate of corrosion when it is present in the corrosion system at an appropriate concentration, without significantly changing the concentration of any other corrosion agent.

Based on the electrochemical mechanism of action, corrosion inhibitor additives can be classified into three types:(a) anodic,

(b) cathodic and (c) mixed, depending on whether they affect the anodic reaction, the cathodic reaction or both [20].

2.3 Anodic inhibitors

An anodic inhibitor causes the formation of a very thin layer on the anodic sites by displaces the potential of corrosion to the passivation zone, which increases the potential of the anode and decreases the rate of corrosion [21]. Anodic inhibitors, mostly oxidizing anions, are effective only when present in sufficiently high concentrations [22].

Nitrates, benzoates, chromates, molybdates, and orthophosphates are used as anodic inhibitors. However, at present, the most used anodic inhibitor for concrete is calcium nitrite [23].

2.4 Cathodic inhibitors

Cathode inhibitors slow down the oxygen reduction reaction on the surface of the steel by precipitating salts with low solubility in water creating a surface barrier that restricts oxygen transport to cathode sites. The reduction in oxygen supply during the corrosion process will result in a decrease in both the potential and the rate of corrosion [24].

Cathode inhibitors may include phosphates, polyphosphates, silicates, or carbonates, and their dosage tends to be relatively high because their efficiency in preventing corrosion is lower compared to that of anodic inhibitors [25].

2.5 Mixed inhibitors

Mixed inhibitors are composed of mixtures of organic components, such as amino alcohols, amines, and amino acids, or by emulsions of unsaturated fatty acid esters [26], hence the reason why these inhibitors are also known as organic inhibitors. The mechanism of action of these inhibitors is based on adsorption on the surface of the metal, forming an organic layer, which allows inhibiting anodic and cathodic reactions [27].

The addition of these corrosion inhibitors to the concrete not only allows to decrease the rate of corrosion once it has finally begun, but they also lead to an increase in the threshold content of chlorides lengthening the period of initiation of corrosion.

Unlike inorganic inhibitors (anodic and cathode), whose efficiency is decreased when the doses are very low or before a severe cracking on the surface of the concrete, organic inhibitors give a better behavior under such conditions, being one of their main advantages.

III. PREDICTION OF SERVICE LIFE IN CONCRETE STRUCTURES

According to Reference [28], the service life of reinforced concrete structures affected by corrosion can be divided into two stages: one of initiation (ti) and another of propagation (tp). Namely, either by carbonation or by diffusion of chlorides, the total time (tL) required so that the level of degradation in the structure is such that it compromises its safety or functionality, is expressed as (1):

$$t_L = t_i + t_p \qquad (1)$$

The initiation phase represents the period it takes for chloride ions to penetrate the concrete coating and reach the chloride threshold content on the surface of the steel causing the removal of the passive layer. This critical chloride content is not a specific value but depends on countless factors such as the aggressiveness of the environment, the ratio a/c, the type of cement used, the presence of cracks in the surface, the impurities present in the concrete, and the state of the steel surface [29].

Because it is not a single value, we have tried to determine experimental values of the chloride threshold, obtaining very uneven results [30]. In view of this, conservatively, values of 0.2 to 0.4% by weight of cement could be considered for the threshold content of chlorides during the prediction of the life cycle of reinforced concrete structures [31] [32].

The penetration of chloride ions into the concrete mass can be carried out through various mechanisms, with capillary absorption and diffusion influencing the greatest capacity [33]. However, capillary absorption reaches depths no greater than 1 centimeter when interrupted by the discontinuity of the pore network of the concrete [34], consequently, diffusion is responsible for most of the process.

The phenomenon of diffusion can be analyzed using Fick's Second Law. It is expressed mathematically as presented in equation (2):

$$\frac{\partial c}{\partial t} = D \cdot \frac{\partial^2 c}{\partial^2 x} \qquad (2)$$

where C is the chloride concentration, t is the time, D is the apparent diffusion coefficient and x is the depth from the exposed surface.

Considering the chloride diffusion coefficients is a function of both time and temperature, the software uses the following relationship to account for time-dependent variations in diffusion (3):

$$D(t) = D_{ref} \cdot \left(\frac{t_{ref}}{t}\right)^m \qquad (3)$$

where D(t) is the diffusion coefficient at a given time, Dref is the reference diffusion coefficient for a reference time (tref) of 28 days and m is a constant representing the diffusion variation index. The software selects values of Dref and m based on the composition of the concrete mixture provided entered by the user [35]. To prevent the diffusion coefficient from continuously decreasing over time, the relationship shown in Eq. (2) is assumed to only be valid for up to 25 years [35].

On the other hand, to consider the effect of temperature changes over time, the software considers the following equation (4):

$$D(T) = D_{ref} \cdot exp\left[\frac{U}{R} \cdot \left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \quad (4)$$

Where D(T) is the diffusion coefficient at a time t and temperature T, Dref is the reference diffusion coefficient for a reference time (tref) of 28 days and for a reference temperature (Tref) of 20 [°C], U is the activation energy of the diffusion process (35,000 J/mol) and R is the gas constant. These parameters are considered in the Equation [4].

The software calculates the initiation time (to) of corrosion using a finite difference implementation of Eq. (2), where the value of the diffusion coefficient (D) will be a function of Eq. (3) and (4).

The depassivation of steel marks the end of the initiation stage and the beginning of the propagation stage (Figure 2). This stage lasts until the structure reaches a limit state beyond which the consequences of corrosion can no longer be tolerated [36]. And usually, these consequences are directly related to the appearance of cracks since they compromise the state of service of the structure. The most important parameter to describe the spread of corrosion is corrosion rate, which is highly influenced by oxygen availability (O_2), the electrical strength of concrete, and environmental conditions such as temperature and relative moisture [37].

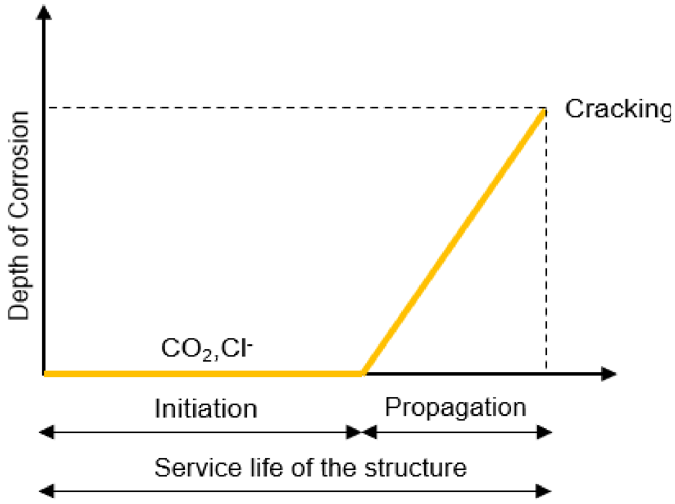

Fig. 2 Prediction of the service life of reinforced concrete structures [28].

3.1. Life Cycle Analysis for Concrete Structures with Corrosion Inhibitors

In any engineering project, it will always be essential to consider the economic aspect for the choice of the different alternatives that are proposed as a solution to the project and where usually the system that provides the greatest economic benefits predominates. Therefore, from the initial design and planning phases, all costs related not only to the construction of the project must be evaluated, but also the costs derived from protection and maintenance strategies must be included, even more so when it is certain that factors that may affect its durability will be witnessed.

Corrosion of steel trusses represents one of the most significant deterioration problems for reinforced concrete structures and they incur excessive maintenance and repair costs. However, as discussed in previous sections, its economic impact can be minimized using new technologies and materials such as corrosion inhibitor additives.

There is little research to determine the costs associated with the implementation of corrosion inhibitors in concrete constructions throughout their life cycle. Most focus on considering only the initial costs of construction including the addition of inhibitors and compare them to the benefits they can bestow on the durability of the structure. Therefore, it is shown that these materials prolong the useful life of the structure, but there is no clear understanding if they represent a cost-benefit for the rest of the phases of the life cycle of the project [38].

Reference [39] specifies five phases that must be considered for the life cycle of a product or service: 1) extraction of raw material, 2) production of materials and inputs, 3) distribution of materials 4) use of materials and 5) end of use/end of life. These phases apply to any reinforced concrete structure, however, to perform a life cycle cost analysis, a more simplified approach could be given and consider three stages: 1) construction, 2) service and 3) end of life of the structure. These are exemplified in Figure 3.

Therefore, to correctly estimate the economic effects of adding corrosion inhibitors to concrete structures, the costs for each of the described stages of the life cycle must be associated (Figure 3). That is, in the first stage, the costs cover all the raw materials and resources used for the construction of the structure. For the second stage, which involves the entire period of occupation that the structure will cover, the costs will depend on the maintenance or repair interventions that are required according to the severity of the damage caused during that period. And finally, in the third stage, when the levels of damage to the structure reach a degradation limit such that its repair is no longer possible or economically viable, it is considered that it has reached the culmination of its useful life, therefore its demolition and with it, the costs will be reflected in the disposal of waste or recycling.

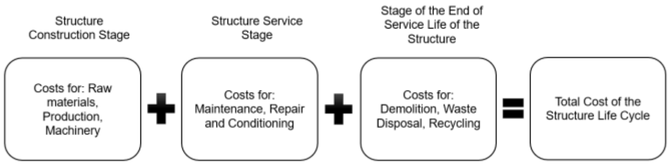

Fig. 2 Diagram of the life cycle cost analysis of a reinforced concrete structure.

IV. CASE STUDIES

The case studies presented in the research were obtained thanks to the collaboration of the designers of each project, Table I details the name of the project, the resistance used in the concrete, the location, and the price per cubic meter.

TABLE I
CASE STUDIES INFORMATION

Case Studies	Location	f'c [kg/cm^2]	Price per [m^3]
Txopituna Building	Manta	300	$ 198.08
Condominium Torre 5	Manta	240	$164.36
Residence Barcía Torres	Manta	210	$158.38
Zambrano Arroyave Family	Daule	210	$158.38

Table II presents the parameters used in the software such as the case study, the element analyzed, the water-cement ratio, the coating to the face of the longitudinal rod and the percentage of steel required in each case.

TABLE II
INCOME PARAMETERS FOR THE SOFTWARE SERVICE LIFE.

Case Studies	Analysis element	a/c	Rec. [cm]	ρ (%)
Txopituna Building	Column	0,4	6	1,03
Condominium Torre 5	Flagstone	0,47	2	0,4
Residence Barcía Torres	Wall	0,51	4	0,55
Zambrano Arroyave Family	Flagstone	0,51	2,5	0,25

The temperature tables used for the three cases of studies located in the city of Manta and Daule were obtained from nearby localities, because there are no meteorological stations on the site as such, these values were extracted from the meteorological yearbook of INAMHI (Instituto Nacional de Meteorología e Hidrología.) and they are presented in Table III and Table 4.

TABLE 1

AVERAGE TEMPERATURES FOR THE CITY OF PORTOVIEJO

Portoviejo	
Month	T_{prom} [ºC]
January	25,3
February	25,6
March	26,5
April	26,7
May	26,7
June	25,6
July	24,4
August	24,2
September	24,4
October	24,6
November	25,0
December	25,7

TABLE 2
AVERAGE TEMPERATURES FOR THE CITY OF NOBOL.

Nobol	
Month	T_{prom} [ºC]
January	26,2
February	26,4
March	26,8
April	26,8
May	25,9
June	24,7
July	24,0
August	24,9
September	25,7
October	25,9
November	25,9
December	27,0

The values of maximum concentrations of chlorides at the surface (Cs) and the maximum time (to max) at which that concentration is reached used for in the three cases of studies located in Manta were taken in a similar way to those of the city of San Francisco in the USA due to their environmental similarities. The values of Ct are a function of the weight of the concrete that is used, this factor varies depending on the inhibitor and the content of the same used in the simulations.

The diffusion values of chlorides (D) depend on the water-cement ratio, the default values were used in the program, it should be noted that these were obtained from tests with cementitious material other than Portland of general use in Ecuador (Table V).

TABLE V
MAXIMUM CONCENTRATIONS OF CHLORIDES AT THE SURFACE, CRITICAL CONCENTRATIONS OF CHLORIDES, MAXIMUM TIMES, AND COEFFICIENTS OF DIFFUSION OF CHLORIDES.

Case Studies	C_s (%)	C_t (%)	$t_{o\ max}$ [years]	D [m^2/s]
Txopituna Building	0,6	0,05	15	$7.94*10^{-12}$
Condominium Torre 5	0,6	0,05	30	$1.17*10^{-11}$
Residence Barcía Torres	0,6	0,05	15	$1.46*10^{-11}$
Zambrano Arroyave Family	0,6	0,05	15	$1.46*10^{-11}$

The propagation period is 6 years taken from the software manual reference. The default inflation percentage is 1.8% which will be used to project the future cost.

For the analysis of the life cycle cost of the section chosen in each case study, a reference value for the repair process of $250.28 per square meter and the application of an organic inhibitor based on amines and ethers was considered, which had a value of $22.40 per liter.

V. ANALYSIS AND RESULTS

For each case study, two concrete mixtures were analyzed: a mixture without corrosion inhibitor (Alternative 1) and another with the presence of this product (Alternative 2) with a dosage of 5 liters/m^3, to evaluate the effects produced by the inhibitor on the durability of reinforced concrete structures.

The Figure 4 show represents the variation of the concentration of chlorides on the surface of the reinforcing steel as the exposure time varies, this graph propagates until reaching the concentration of chlorides Ct, which indicates the beginning of corrosion of the reinforcing steel. This graph corresponds to the first case study, the column section of the Txopituna building.

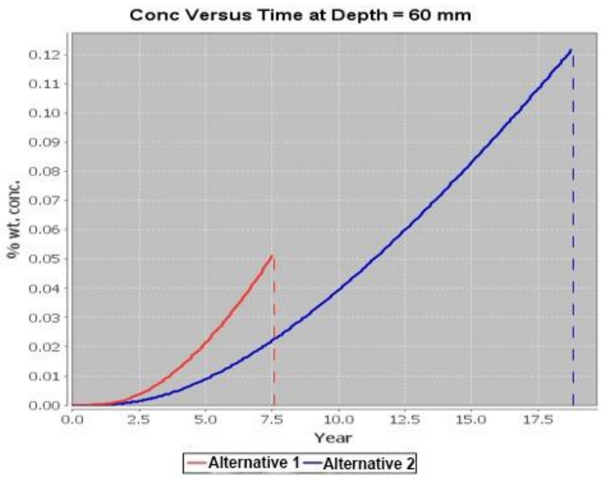

Fig. 3 Variation in chloride concentration.

It can be seen in the graph above that the application of the corrosion inhibitor (Alternative 2) increases the Ct concentration up to a value of 0.12% of the weight of the concrete, obtaining a longer initiation period, since the chloride ions require reaching a much higher Ct concentration than Alternative 1 (without corrosion inhibitor).

About the cost analysis, it can see in Figure 5 the useful cost of life of the section chosen in this case study, it should be noted that Alternative 2, which had the application of the corrosion inhibitor, presents a higher construction cost however, because it has a longer initiation period, it ends up needing fewer interventions for repair, unlike Alternative 1.

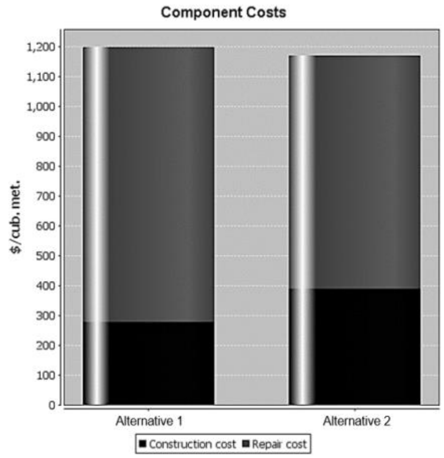

Fig. 5 Components of the total life cycle cost.

In the Figure 6 it can see how Alternative 1 presents a total cost of $1198.92 per m^3 of concrete at the end of the analysis period, while Alternative 2 presents a total cost of $1169.97 per m^3 of concrete at the end of the 75 years of analysis. This variation in the final cost represents a saving of 2.47% when choosing Alternative 2 compared to Alternative 1.

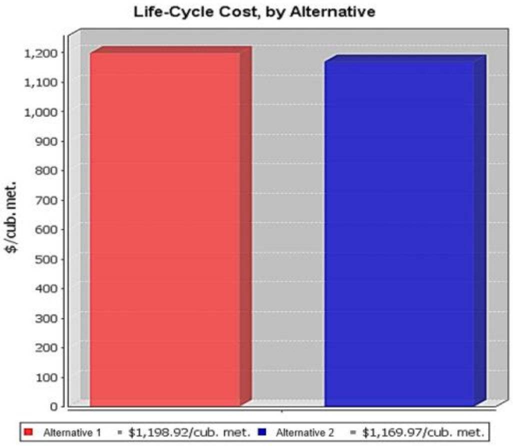

Fig. 4 Lifecycle Cost

The Table VI show the life cycle cost analysis for each case study, it should be noted that for the third and fourth case no appreciable and even no percentage savings were obtained, and this occurs because the corrosion inhibitor is generally effective for structures with cement water ratio less than 0.50. For elements with higher water/cement ratios it does not turn out to be economically effective.

TABLE VI

LIFE CYCLE COST ANALYSIS.

	Life-Cycle Cost			
	Txopituna Building	Condominium Torre 5	Residence Barcía Torres	Zambrano Arroyave Family
Without Inhibitor	$ 1,198.92	$ 1,812.80	$ 1,009.98	$ 827.45
With Inhibitor	$ 1,169.97	$ 1,671.80	$ 1,000.96	$ 843.26
Savings percentage	2.47%	8.43%	0.90%	-1.87%

The variation of the life cycle cost of each case study applying two alternatives: with corrosion inhibitor additive and without corrosion inhibitor additive can be observed Figure 7.

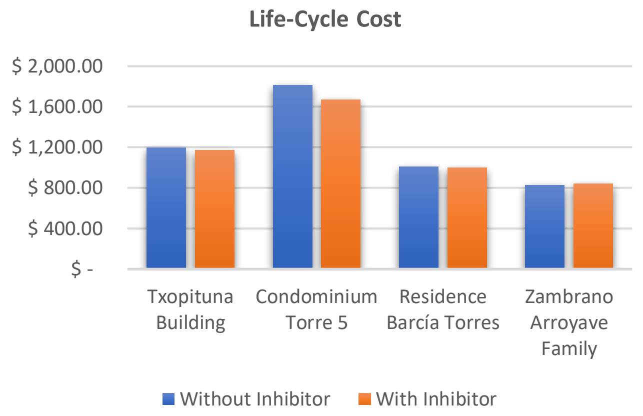

Fig. 7 Comparison of the life cycle cost of structures with and without inhibitors of each case study

VI. CONCLUSIONS

The use of corrosion inhibitors has a positive impact on most reinforced concrete structures, the structures that receive an improvement in their performance are those that work with a water/cement ratio less than 0.5 because the cost-benefit ratio through their useful life becomes evident.

The inhibitor that presented the best performance was the inhibitor-based on amines and ethers, to reach this conclusion the shelf life and its impact on the environment were considered.

The diffusion of chlorides in reinforced concrete elements simulated in the program is calculated using experimental equations based on data from laboratory tests carried out in the countries of North America, therefore this value would present some changes in Ecuador, mainly due to the composition of the local cement, which compared to the Portland cement, it has a percentage of additional cementitious materials that improve the performance of the mixture against corrosion.

Among the parameters that generate the highest incidence in the period of the useful life of a reinforced concrete structure against corrosion is the coating of the section because a greater coating considering the same diffusion of chlorides, generates an increase in the initiation period.

For the analysis of the propagation period, a reference value was considered based on experimental tests, however, this period can be estimated considering the loss of the reinforcement section of the structure as it corrodes, until reaching a certain period where the structure does not meet the minimum service criteria and must proceed to its repair.

The Service Life 365 software provides greater ease when calculating the useful life period, however within the methodology of this program it can be concluded that there are many limitations such as the consideration of rectangular sections for more exhaustive cost analysis, and the incorporation of relative humidity values and average wind speed that provide results with a greater approximation to those expected in real life.

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