NUEVAS TENDENCIAS EN EL SISTEMA DE ADITIVOS INHIBIDORES DE LA CORROSION PARA CONCRETO REFORZADO

por

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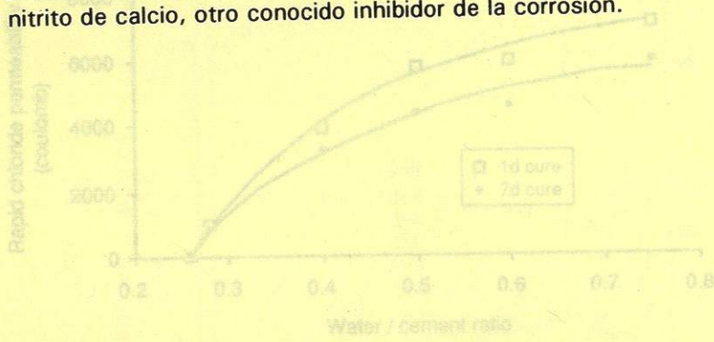
Sinopsis: Los Aditivos Orgánicos Inhibidores de la Corrosión (OCIA) se están estableciendo rápidamente como un método efectivo para inhibir la corrosión del acero en el concreto reforzado. Este trabajo presenta un amplio resumen de los sistemas para inhibir la corrosión del concreto reforzado, incluyendo los Aditivos Orgánicos Inhibidores de la Corrosión.

Uno de tales OCIA funciona por medio de un mecanismo protector doble, el cual inhibe el ingreso de cloruros y humedad en el concreto y forma una delgada barrera protectora en el acero de refuerzo.

El trabajo detalla los procedimientos de ensaye y resultados de una prueba independiente del tiempo necesario para la corrosión llevado a cabo sobre este OCIA, en particular, el cual indica que su comportamiento es igual o mejor que 2, 4 y hasta 6 galones de nitrito de calcio, otro conocido inhibidor de la corrosión.



Palabras clave: Corrosión, inhibidor de la corrosión, sistema inhibidor de la corrosión, evaluación, aditivo orgánico inhibidor de la corrosión, OCIA, ensaye de corrosión a vigas preagrietadas, tiempo necesario para la corrosión, ensaye de corrosión a vigas no agrietadas.

NEW DEVELOPMENTS IN CORROSION INHIBITING ADMIXTURE SYSTEMS FOR REINFORCED CONCRETE

By

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Synopsis: Organic Corrosion Inhibiting Admixtures (OCIA) are rapidly becoming established as an effective method of inhibiting corrosion in steel reinforced concrete. The paper presents a comprehensive summary of corrosion inhibiting systems for reinforced concrete, including Organic Corrosion Inhibiting Admixtures.

One such OCIA functions by way of a dual protective mechanism which inhibits the ingress of chlorides and moisture into the concrete, and forms a protective barrier film on the reinforcing steel.

The paper details the test procedures and results of independent time-to-corrosion tests performed on this particular OCIA, which indicate that it performs as well or better than 2, 4 and up to 6 gallons of calcium nitrite, another known corrosion inhibitor.

Keywords: corrosion; corrosion inhibitor; corrosion inhibiting system; Evaluation; organic corrosion inhibiting admixture; OCIA; Precracked Beam Corrosion test; time-to-corrosion; Uncracked Beam Corrosion test;

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INTRODUCTION

"Our infrastructure is crumbling!" These words are being heard with increas regularity, and refer to the devastating effects of corrosion on the massive quantities concrete and steel that support our nation's buildings, bridges, and other structure Indeed, corrosion has become the number one enemy in our struggle to maximize t useful life of these structures.

The cost of corrosion in terms of loss of use and cost of repairs is staggering. Approximately 42 percent of all bridges in the United States are classified as structura deficient or functionally obsolete by the Federal Highway Administration (1). More th 130,000 of the nations 575,600 bridges restrict the weight of trucks passing over the and about 5,000 have been closed (2).

The cost to repair the bridges alone is estimated at about $90 billion (2). Add to t the cost of repairing the multitude of buildings, highways, parking garages, and ot structures damaged by corrosion and the estimate reaches $258 billion, almost 6% of t national debt.[1]

In reinforced concrete, corrosion occurs when moisture, oxygen, and chlorides w their way through the concrete cover to react with the reinforcing steel. This reac causes the reinforcing steel to deteriorate, and causes ferric oxide to build up within t concrete. As the volume of ferric oxide increases, it creates intense outward pressure the concrete causing it to crack and spall.

Once the reinforcing steel begins to corrode, the process accelerates. The cracking spilling allow even greater quantities of chlorides and moisture to reach the reinforc steel. In addition, the portions of reinforcing steel under the most stress corrode m rapidly, and stress concentrations increase as the reinforcing steel deteriorates. U unrepaired, the load bearing capacities of the concrete and reinforcing steel will eventu be reduced, making them susceptible to further damage from the effects of structural lo and heavy traffic.

[1]National Association of Corrosion Engineers, 1993.

CORROSION INHIBITING SYSTEMS

Due to the growing costs resulting from corrosion damage, more attention is being paid to the design of reinforced concrete structures exposed to moisture and chlorides, as well as to the materials being used to build them.

ACI 116R-85 defines a corrosion inhibitor as, "a chemical compound, either liquid or powder, that effectively decreases corrosion of steel reinforcement before being embedded in concrete, or in hardened concrete if introduced, usually in very small concentrations, as an admixture."

The National Association of Corrosion Engineers (NACE) further defines corrosion inhibitors as, "a substance which, when added to an environment, decreases the rate of attack by the environment on a metal (3)."

The reinforcing steel in portland cement concrete is protected by a passive iron oxide layer that forms because of the high pH of the concrete. As long as there are no breaks in this passive layer, corrosion will not occur. Thus, most corrosion inhibitors work by reinforcing the passive layer or preventing outside agents from reacting with it.

There are several systems currently used to combat corrosion. These systems work at three different levels: a) at the exposed surface of the concrete by closing the pores and prohibiting the penetration of moisture, oxygen and chlorides into the concrete; b) within the concrete by making the it denser, thus making it more difficult for the moisture and chloride to reach the reinforcing steel; c) at the reinforcing steel level by insulating the reinforcing steel from chlorides and moisture.

Membranes and sealers are surface methods commonly used to combat corrosion. These are applied to the concrete surface to seal the pores and prevent the entrance of moisture and chlorides into the concrete. Membranes, which may be urethanes, neoprenes, or epoxies, are usually built up in multiple layers. Membranes can be extremely effective, but must be protected from being damaged in service, and are typically quite expensive.

Sealers range from linseed oil to silanes and siloxanes. For penetrating sealers to be effective over the life of the structure, they must be reapplied periodically due to their exposure to abrasion and weathering.

Epoxy-coated reinforcing steel bars are a corrosion inhibiting system that works to insulate the reinforcing steel from corrosion causing agents. This system consists of precleaned steel bars protected with a coating of powdered epoxy that is fusion-bonded to the steel in an assembly line process. However, damage to the epoxy coating may occur during handling and placement (especially when the reinforcing steel is bent) resulting in an exposed area on the steel where the chloride ions can initiate the corrosion reaction. The effectiveness of epoxy coated steel is the subject of much debate, and is being increasingly questioned.

There are various methods available that work within the concrete to inhibit corrosion. These include low water/cement ration, increased cement content, no-slump concrete, silica fume, and corrosion inhibiting admixtures. These methods work in distinct ways and provide varying degrees of protection.

Cathodic protection can also be used to inhibit corrosion. However, due to the high cost of this system, it is typically used only in small areas of new construction or for preventing further corrosion of an existing structure in need of repair.

Good concrete practices including a low water-cement ratio, adequate cover over the reinforcing steel, sufficient curing, and the use of post-tensioning to minimize cracking are essential in any effort to minimize or eliminate corrosion. Unfortunately, while good concreting practices are essential, they alone will not prevent corrosion.

No-slump concrete is concrete proportioned with a very low water-cement ratio (usually 0.35 or below, containing about 800 lbs/ yd^3 of cement) and is a low cost corrosion inhibition approach. No-slump concrete's effectiveness as a corrosion inhibitor is based upon its relative impermeability, and its performance is fair to good. However, it is extremely difficult to place and has limited applications.

Silica fume is an effective pozzolanic material that reacts with calcium hydroxide in hydrated portland cement to form additional cementitious material. Silica fume particles are many times smaller than those of cement. The silica fume particles fill the spaces between the cement particles making the concrete significantly denser and less permeable. Due to the increased density, special attention must be given to the curing and finishing stages of placement. While the cost of silica fume concrete is in the medium range, its performance is good to excellent in delaying or preventing the corrosion process.

Cathodic protection applies an external source of direct current to the reinforcing steel in the concrete, thus "short circuiting" the corrosion process and controlling corrosion. In cathodic protection, a metallic anode is embedded in the concrete and an electric current is applied. The introduction of the electric current forces the entire structure to become cathodic. Since corrosion takes place only at anodic locations, the corrosion process is stopped. Cathodic protection has high initial costs, but low to medium operating costs. It is viewed as a complicated process because of its preinstallation engineering and post installation monitoring. However, it provides excellent corrosion protection.

Until the introduction of Organic Corrosion Inhibiting Admixtures, calcium nitrite was the only corrosion inhibiting admixture available. Calcium nitrite is an inorganic corrosion inhibitor which reacts with ferrous ions from the reinforcing steel to reinforce the passive layer. In this reaction the nitrite ions compete with any chloride ions present to react with the free ferrous ions.

The relative amounts of chloride and nitrite available at the reinforcing steel determine whether the ferrous ions react with the chlorides or the nitrites. If there are more chlorides

present than nitrite, the ferrous ions will react with the chloride and begin the corrosion process. If there are more nitrites than chlorides, the passive layer will be reinforced.

For calcium nitrite to be effective, the dosage of calcium nitrite must be determined based upon the anticipated chloride loading of the structure over its expected design life. Accurately determining lifetime chloride levels is difficult and subject to many variables.

ORGANIC CORROSION INHIBITING ADMIXTURES

Organic Corrosion Inhibiting Admixtures are the most recent development in the battle against corrosion. OCIA's have rapidly become established as an extremely effective and cost efficient method of inhibiting corrosion in steel reinforced concrete.

One such OCIA is a water-based organic admixture consisting of amines and esters. This particular OCIA functions through a dual protective mechanism to inhibit corrosion in steel reinforced concrete structures. The first protective mechanism functions by inhibiting the ingress of chloride ions into the concrete. This "screening" effect inhibits corrosion by reducing the amount of moisture and chlorides that are able to reach and react with the reinforcing steel.

The second mechanism through which this particular OCIA inhibits corrosion is the formation of a barrier film on the reinforcing steel. Components of the OCIA bond to the reinforcing steel by adsorption, and establish a barrier to the electrochemical attack of corrosion causing agents.

EVALUATIONS

The effectiveness of this OCIA, as well as its compatibility in concrete have been proven through independent testing. Accelerated corrosion tests and standard concrete compatibility tests were used in the evaluation.

An independent laboratory was commissioned to thoroughly evaluate the corrosion inhibiting properties of the OCIA. Three time-to-corrosion test procedures were performed; Uncracked Beam, Precracked Beam, and ASTM G-109. Concrete mixes containing one gal/ yd^3 of the OCIA were tested against a control mix and mixes containing 2, 4, and 6 gallons/ yd^3 of calcium nitrite.

Uncracked Beam Corrosion Tests- Procedure

The Uncracked Beam Corrosion test is an accelerated test that evaluates the corrosion of reinforcing steel in concrete over a 48 week period. The test simulates the exposure of a steel reinforced concrete structure to chlorides, in an accelerated time frame.

Concrete slabs measuring 12 x 12 x 7 in. are cast containing six (6), 1/2 in. (No.4) reinforcing steel bars. Two of the reinforcing bars are placed near the top of the slab with 1 inch of concrete cover. The remaining four bars are placed one inch from the bottom of the test slab. The top bars act as an anode and are where the corrosion takes place.

In order to accelerate the corrosion of the reinforcing steel, chloride ingress is facilitated by the use of moderate to low quality air entrained concrete, a w/c of 0.5, limited curing, and a nominal compressive strength of 5,000 psi at 28 days.

After the slabs are moist cured for 3 days, and air dried for 21, a Lucite dike is attached to the top and the slabs are coated with an epoxy sealer. A 10-ohm resistor is connected between the top and bottom bars.

The corrosion testing begins when the slabs are 28 days old. The slabs are ponded for 4 days with a 15 percent sodium chloride solution at 60 to 80 F. The solution is then vacuumed off and the slabs are air dried at 100 F for three days. This weekly ponding/ drying cycle continues for 48 weeks.

As the test progresses, moisture and chlorides from the salt solution eventually come in contact with the top reinforcing bars and the corrosion process begins. The corrosion of these bars is monitored by measuring electrical potentials at the top reinforcing bars, and the macro-cell corrosion currents generated between the top (anodic) and bottom (cathodic) reinforcing bars.

Corrosion currents are used to measure of the amount of corrosion occurring on the reinforcing steel. The greater the current, the greater the amount of corrosion that is occurring.

Electrical potentials are another measure of corrosion activity. Researchers for the Federal Highway Administration have determined that, "...corrosion activity starts at a half-cell potential of about -0.24 volts... Active corrosion occurred at half-cell potentials as low as -0.20 to -0.25 volts and that significant corrosion current developed in the "uncertain range," i.e. -0.25 to -0.35 volts, as discussed in ASTM C876 (6)."

In addition to measuring corrosion current and half-cell potentials, the chloride content of each slab is measured at the upper reinforcing steel level when corrosion is first initiated, and again after the 48 week test is completed.

Uncracked Beam Corrosion Tests- Results

Results from the Uncracked Beam Corrosion tests show that the OCIA most effectively inhibited corrosion as compared to the control mixes and those mixes containing up to 6 gal/ yd³ of calcium nitrite. The results of the Uncracked Beam Corrosion tests are shown in Table 1.

Figure 1 shows that on average specimens containing the OCIA were the last of the mixes to initiate corrosion (at about 19 weeks). The macro cell corrosion current was also the lowest in specimens containing the OCIA. This indicates that the OCIA effectively reduced the rate of corrosion once it was initiated.

The test specimens of control concrete as well as those containing calcium nitrite at 2 gal/ yd³ initiated corrosion between 7 and 12 weeks. Specimens containing 4 gal/ yd³ of calcium nitrite began corroding at 8 and 26 weeks. One slab containing calcium nitrite at 6 gal/ yd³ initiated corrosion in the 19th week of testing. In, one specimen containing the OCIA at 1 gal/ yd³, corrosion was not initiated until the 22nd week of the test. By the end of the 48 week test period, the companion slabs for the OCIA at 1 gal/ yd³ and calcium nitrite at 6 gal/ yd³ had not yet started to corrode.

The corrosion current generated by each specimen was monitored throughout the test. The average corrosion current of the control mixes and those containing calcium nitrite at 2 gal/ yd³ exceeded that of the calcium nitrite at 4 gal/ yd³ at approximately 10 weeks. The corrosion current generated by the single specimens treated with the OCIA at 1 gal/ yd³ and calcium nitrite at 6 gal/ yd³ remained very low throughout the test, and was significantly lower than the other specimens.

At the end of the 48 week test period, each specimen was vertically sawcut approximately 1 in. from the edge of the top bars to identify any corrosion induced delaminations. The control specimens showed delaminations 9 and 4 in. long. Slabs containing 2 gal/ yd³ of calcium nitrite both contained delaminations. However, one of the specimens was damaged before the delamination could be measured. The delamination on the other specimen was 4 in. long. Of the slabs containing 4 gal/ yd³, one contained a delamination of 6 in., while the other showed none. Finally, none of the OCIA slabs, nor the calcium nitrite slabs at 6 gal/ yd³ contained any delaminations.

After the initial vertical sawcut, the top concrete cover was removed to reveal the length of any corrosion that had taken place, and the overall condition of the reinforcing steel. The two top pieces of reinforcing steel were examined from each specimen, equating to four pieces of reinforcing steel per mix. The average corroded length of the four pieces of reinforcing steel for each mix is shown below.

Mix	Avg. corrosion length	Severity
1 gal OCIA	1.1 in.	Very light to minor
Control	5.6 in.	Severe
2 gal calcium nitrite	6.1 in.	Moderate to severe
4 gal calcium nitrite	2.1 in.	Very light to severe
6 gal calcium nitrite	1.1 in.	Very light to moderate

The reinforcing steel removed from the concrete specimens containing 1 gal/ yd³ of the OCIA were shown to contain only very light to minor scale- Evidence that only minor corrosion activity had occurred. In the control specimen, severe pitting was evidenced on all of the reinforcing steel. The length of corrosion in the control mix ranged from 3.25 in. to 9 in.. Moderate to severe pitting was also evident in all of the reinforcing steel taken from the specimens containing calcium nitrite at 2 gal/ yd³. The length of corrosion from these specimens ranged from 4 to 7.25 in.

In the slabs containing 4 gal/ yd³ of calcium nitrite, the reinforcing steel showed moderate to severe pitting in two pieces of reinforcing steel, and minor to light scale in the remaining pieces. Moderate pitting was observed in one reinforcing steel specimen from slabs containing calcium nitrite at 6 gal/ yd³ A second specimen contained moderate to severe scale, while the remaining two pieces of reinforcing steel were determined to have very light to minor scale. The length of corrosion and overall reinforcing steel condition are summarized in Table 2.

Precracked Beam Tests- Procedure

The precracked beam corrosion test measures the effectiveness of corrosion inhibitors in cracked concrete. While the specimens for this test were cast using the same concrete mix as was used in the standard Uncracked Beam Corrosion test, the Precracked Beam Corrosion test is more severe since chlorides and moisture have direct access to the reinforcing steel.

In this test method, 4x5x16 in. specimens were cast with one No.3 reinforcing steel bar placed near the top the specimen, and two No. 3 reinforcing bars placed near the bottom surface. The cover for the top and bottom reinforcing steel is 1 in.

The test slabs were moist cured for 7 days, then air dried for 14 days. The specimens were then stressed under center point flexure to induce a stress crack with a width at the top of the specimen of approximately 0.010 in. Steel plates were attached to the sides of the slabs to prevent the crack from closing. After the cracking procedure had been completed, the final surface crack width was verified to be between 0.008 to 0.010 in.

Once again, Lucite dikes were attached to the top of the test specimens, and a 10-ohm resistor was connected between the top and bottom reinforcing steel.

Corrosion testing began when the slabs were 28 days old. The specimens were ponded for 4 days with a 6 percent sodium chloride/ water solution at 60 to 80 F. The solution was then vacuumed off, and the slabs dried for 3 days at 60 to 80 F. This cycle continued for 23 weeks.

Precracked Beam Tests- Results

At the conclusion of the test period, only one specimen out of six containing the OCIA at 1 gal/ yd³ exceeded 100 uA of current. All of the specimens of the control mix, and of

calcium nitrite at 2 gal/ yd³ and 6 gal/ yd³ showed corrosion current in excess of 100 uA. Four of the six reinforcing steels from the specimens containing calcium nitrite at 4 gal/ yd³ exceeded 100 uA.

In analyzing the test results, the control specimens and specimens containing 2 gal/ yd³ of calcium nitrite had the highest average corrosion currents. They also had the most negative half-cell potentials. The test slabs containing the OCIA at 1 gal/ yd³ took the longest to initiate corrosion, and had the lowest corrosion currents during the test period. Corrosion currents from the specimens containing 4 and 6 gal/ yd³ of calcium nitrite were less than the control mix, but greater than those containing the OCIA. The average corrosion current in the specimens containing calcium nitrite at 6 gal/ yd³ increased significantly after 20 weeks, and was equivalent to those currents from the specimens containing 2 gal/ yd³ of calcium nitrite.

Results from the half-cell potential readings were similar. Specimens containing the OCIA and calcium nitrite at 6 gal/ yd³ had similar readings which were less negative than any of the other mixes. The control mix and the mix containing 2 gal/ yd³ of calcium nitrite had the most negative half-cell potential readings.

At the conclusion of the 23 week test period, the test slabs were sawcut and the reinforcing steel removed. Most all of the bars had corrosion close to the crack, and several had pitting at the point where the crack met the reinforcing steel. The length of corrosion was then measured, and the average corrosion length and the severity are shown below.

Mix	Avg. corrosion length	Severity
1 gal OCIA	2.8 in.	No corrosion to severe
Control	8.1 in.	Severe
2 gal calcium nitrite	11.3 in.	Severe
4 gal calcium nitrite	8.5 in.	Severe
6 gal calcium nitrite	6.8 in.	Moderate severe to very severe

The reinforcing steel removed from the concrete specimens containing 1 gal/ yd³ of the OCIA showed an average corrosion length approximately 65% less than the control specimens, and over 55% less than the specimens containing calcium nitrite at 6 gal/ yd³. The length of corrosion in the OCIA treated specimens ranged from 0.0 to 7.5 in..

In the control specimen, the length of corrosion ranged from 5 to 11 in.. Corrosion was severe on all specimens. Severe corrosion was also evident in all of the reinforcing steel taken from the specimens containing calcium nitrite at 2 gal/ yd³ The length of corrosion from these specimens ranged from 5.0 to 15.0 in.. In the slabs containing 4 gal/ yd³ of