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Long-term performance of ZnO as a rebar corrosion inhibitor

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Abstract

This paper compares the action of ZnO with $Ca(NO_2)_2$, examines the effect of the w/c ratio on the performance of both inhibitors and how they affect the physical–chemical properties of concrete. To study that effect, 244 probes were prepared with tap water and water from Maracaibo lake (≅3000 ppm Cl^-), and exposed to saline environment for more than two years. Water/cement ratios were 0.45, 0.5 and 0.6, with inhibitor concentrations of 2%, 3% and 4% and a mixture of both at 2%, all by cement weight. The results indicate that ZnO and its mixture with $Ca(NO_2)_2$ show better performance than $Ca(NO_2)_2$. In spite of the higher corrosion rates ($i_{corr} > 0.1$ μA/cm^2) of the ZnO probes (w/c = 0.45), the potentials values ($E > -200$ mV vs. $Cu/CuSO_4$) and the cyclic polarization curves show passivation of the steel after more than two years' exposure to the aggressive environment. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Corrosion; Reinforced concrete; Inhibitors; Zinc oxide; Calcium nitrite

1. Introduction

Proper design and preparation of concrete in accordance with ACI [1] standards and timely maintenance of the structures under those conditions would guarantee them a long and efficient life in aggressive media. However, these requirements are not always met and adhered to. In civil construction, therefore, there have always been corrosion problems in reinforcements, both in structures erected near coasts, quays, ports, bridges, etc., and in structures in which concrete design and preparation did not follow the appropriate standards. Exposure to aggressive conditions or lack of timely maintenance reduces their useful life, generating high repair and/or rehabilitation costs. In some cases, these structures may even be lost, endangering the life and safety of users.

With current knowledge, the protection methods now available to neutralize the aggressive effects of chlorides introduced while mixing the concrete are reduced to cathodic protection and the use of inhibitors. The use of galvanizing does not seem to offer sufficient guarantees for high chloride contamination. This situation arises in cases where it is necessary to carry out repairs on structures in the splash/wave zone, where appropriate water is not available to prepare the reinforced concrete. This is either because of distance from these sources or unsuitable roads, and/or because the water or aggregates available are contaminated by chlorides. These scenarios would bring about the use of these contaminated components, with the consequent deterioration of the reinforcing steel by corrosion. A viable alternative for controlling the corrosion phenomenon is the use of corrosion inhibitors when preparing the concrete, thereby reducing corrosion rates to technically tolerable levels.

Corrosion inhibitors are compounds that, added or supplied to concrete in small proportions, must be compatible with it, and not cause unwanted reactions or negatively alter its physical properties; besides, they must compete economically with other control methods. From the action standpoint, inhibitors affect the rate of corrosion processes, since they influence the kinetics of the electrochemical reactions that cause these processes by simultaneously retarding either the anodic or cathodic reaction – or both.

Inhibitors are widely used in corrosion technology, but their use for controlling steel corrosion in concrete has been limited due to the different types of environments to which structures are exposed, and to their effect

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on the mechanical and physical–chemical properties of concrete produced by the inhibitor [2–4].

Corrosion inhibitors [2–21] are presented as an attractive option for preventing the corrosion of steel in concrete in the presence of chloride ions. The first patent was awarded to a company in 1977 for commercial application of nitrite-based inhibitor [19].

Of the different inhibiting substances evaluated, appropriate for the alkaline medium in concrete, calcium nitrite has produced the best results, even for cracked concrete [12], so it has been used commercially with relative success. Besides being toxic, calcium nitrite is very costly and difficult to obtain in some countries, so studies of other additives have been undertaken in an effort to replace it, either partially or totally. It has been found that $Ca(NO_2)_2$ improves the corrosion resistance of steel to chloride-ion attacks for w/c ratios < 0.5 [5,15], the w/c ratio being considered as the factor most affecting corrosion. On the contrary, other authors [20] found that corrosion rate varies significantly with the cement type, the minerals used and fine aggregate and, to a lesser degree, with the water/cement ratio. It has also been indicated that, if the durability of the structures is to be guaranteed, the inhibitor must be used in good quality concrete because the characteristics of the different components in the concrete influence durability [16].

Ramirez [21] studied other inhibitors (gluconate, phosphate, urotropine, chromates, resorcinol, fluoroglucinol, and zinc oxide). He did not find any with efficiency comparable to that of the nitrites. He points out, however, that the protection afforded by nitrites is temporary when under immersion, requiring very good quality concrete and very thick covering. In the case of severely corroded reinforcements, nitrite fails to passivate them, so repeated spraying of pre-corroded structures with inhibiting solutions cannot be considered a method of protecting these reinforcements. It has also been shown [21] that NO_2^-/Cl^- is ineffective when the ratio is <1. As $Ca(NO_2)_2$ is an anodic inhibitor, it could become hazardous when its concentration is reduced to levels that would increase the corrosive attack. With immersion, both Cl^- and NO_2^- would also leach out of the concrete because they have similar diffusion coefficients, leaving the same relative proportion of both ions that were present before immersion [21].

Other investigations [22] developed rehabilitation processes for reinforced concrete structures, using four inhibitor formulations: (i) organic inhibitor, which is thought to form a protective film by transformation into a metallic soap; (ii) a mixture of surfactant and amino salts in water, or volatile corrosion inhibitor; (iii) alcanolamine, an additive that would function by migrating and inhibiting in the same way as (ii); and (iv) $Ca(NO_2)_2$. In field application to chloride-contaminated concrete and pre-corroded reinforcements, the results indicate that (ii) and (iii) showed a significant reduction in corrosion rate, and reduction in (i) was lower than (ii) and (iii), whereas $Ca(NO_2)_2$ produced a substantial increase in corrosion rate. The latter result has been obtained in other investigations [21].

On the basis of the foregoing discussion, a good case may be made for the use of $Ca(NO_2)_2$ as a corrosion inhibitor in reinforced concrete structures, given the series of advantages it presents, advantages that make it reliable within the initial and borderline conditions considered. However, for other conditions where nitrite performance is unsatisfactory, further evaluation and a more in-depth study of other inhibitors and application methods are needed. Such is the case with ZnO [4,8,23–25], which has been under study to try and replace nitrite either partially or totally. These results [4] show that the best inhibiting effect is obtained by mixing them in equal concentrations. The behavior of these mixtures in chloride environments was evaluated electrochemically [23] in concrete with w/c ratio $= 0.6$ (conventional concrete mixture used in Venezuela). Results show that the mixture of these inhibitors at 2% is effective during the evaluation period.

It is important to point out that the use of inhibitors in concrete would be economically competitive with other corrosion-control techniques if they were effective in conventional concrete, this being the reason why all the evaluations carried out in Centro de Estudios de Corrosión (CEC) used this type of mixture.

In view of these results and of those obtained with $Ca(NO_2)_2$ – field use of the latter is currently specified together with concrete of excellent quality (w/c $= 0.4$) –, it was decided to evaluate the effect of w/c ratio in the behavior of ZnO and its mixture with $Ca(NO_2)_2$. This work therefore presents a summary of the experimental procedure and the results obtained during the past two years' evaluation.

2. Experimental procedure

A total of 244 concrete probes (Portland cement I) with w/c ratios of 0.45, 0.5 and 0.6 were prepared, using lake water to mix 27 pattern probes (probes with no inhibitor), 190 probes with inhibitor concentrations (ZnO or $Ca(NO_2)_2$) at 2%, 3% and 4% on the basis of cement weight, mixture at 2% (on the same basis) of both inhibitors, and tap water in 27 pattern probes. Of these, 136 probes were used for the electrochemical tests: 81 probes to determine compressive strength (ASTM C-39) and 27 probes to determine porosity (ASTM C-642). The nomenclature is presented in Fig. 1.

With the calcium nitrite solution, a mass balance was carried out to keep the water/cement ratio constant in

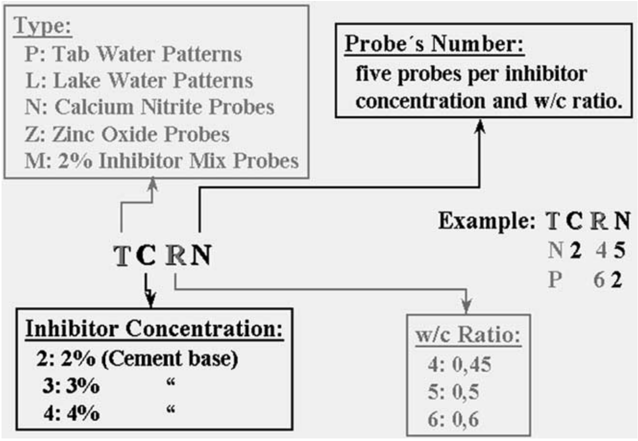

Fig. 1. Nomenclature of the probes.

the mixture, using: the calcium nitrite solution density, the calcium nitrite concentration in the solution (weight/volume percentage), the cement mass to be used for each water/cement ratio, the percentage of inhibitor to be used per cement mass and the amount of water specified for each pattern.

The pattern and nitrite probes were demolded 1 day after preparation. The probes with the mixture ($ZnO/Ca(NO_2)_2$ at 2%) and with ZnO at 2%, 3% and 4% were demolded after 5, 8, 11 and 11 days, respectively, since zinc oxide is a setting retarder. Curing was done in tap water for 28 days. Because of their larger size (15 cm ∅ × 30 cm long cylindrical probes) and ZnO setting-retarding action, curing time was longer (69 and 73 days) for some of the probes (3% and 4% ZnO) used to determine compressive strength.

Fig. 2 shows the arrangement of the probes used to evaluate electrochemical properties (potentials, R_p and potentiodynamic cyclic polarization curves at 0.28 mV/s) of the different mixtures tested. The working electrodes were 0.95 cm (3/8 in.) diameter rebars cut into 10 cm lengths. An epoxy coating was then applied to each end of the rebar, leaving 6 cm uncoated, which is equivalent to approximately 18 cm^2. The coating was inspected at 20× under the stereoscopic microscope, in order to detect and correct any flaws. In all, three layers of coating were applied.

The reference and auxiliary electrodes were made of graphite: Reference: 0.79 cm (5/16 in.) ∅ × 4 cm long; Auxiliary: 0.79 cm (5/16 in.) ∅ × 6 cm long, from copper-coated bars 30.48 cm (12 in.) long. The coating was removed mechanically. These electrodes were later subjected to a chemical treatment designed by CEC [26] to eliminate residues of copper, iron and organic matter.

A hole (0.15 cm (1/16 in.) ∅ and 1 cm deep) was drilled in all the electrodes and an AWG 14 cable (20 cm long) was inserted.. The electrodes were covered with plastic tubing at the cable junction, sealing them with epoxy resin to keep out humidity. Finally, electrical conductivity tests were run to verify good cable–electrode connections.

Once the probes were set, the potentials of the reinforcement steel were measured with a 10 MΩ internal impedance multimeter, using saturated copper–copper-sulfate as the reference electrode. Readings were taken every 2 days for the first 28 days; then, taking the blanks

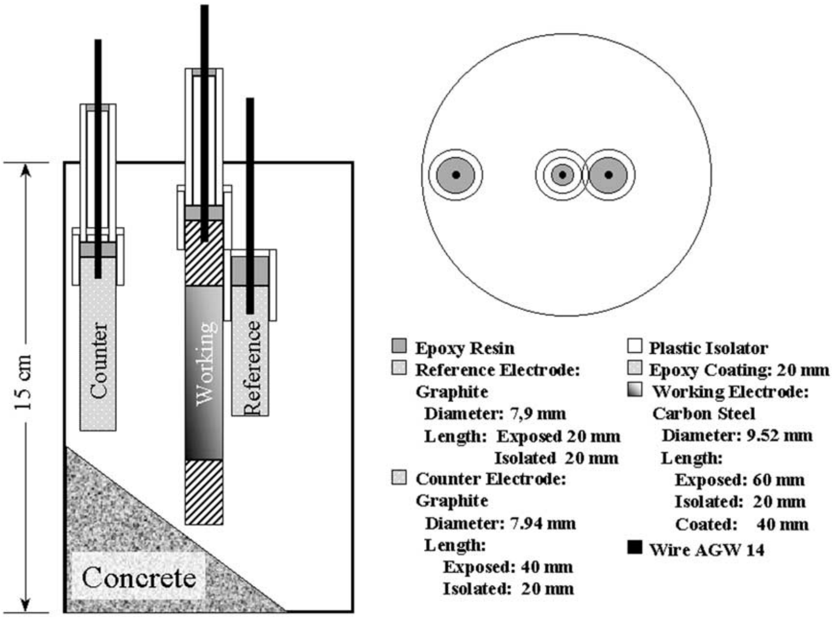

Fig. 2. Details of probes for electrochemical tests.

as reference, twice a week until approximately 147 days had elapsed; finally, once a week until the end of the tests. The values reported are the averages of the potentials measured in each set of probes according to w/c ratio and inhibitor concentration. ASTM C-876-92 was used to determine the active/passive state of the reinforcement.

The linear polarization resistance of the different probes was evaluated at the end of the curing period and approximately every 30 days thereafter at a scan polarization rate of 0.28 mV/s. This was done with a PAR 173 computerized potentiostat and a Model 276 interface. These tests were run to determine the corrosion rate with the Stern and Geary equation [27]: ($i_{\mathrm{corr}} = B/R_{\mathrm{p}}$). The values reported are the averages of the polarization resistance measured in each set of probes according to w/c ratio and inhibitor concentration.

Cyclic polarization curves were obtained for one of the probes of each inhibitor concentration and w/c ratio after the curing period and whenever the potential and polarization resistance measurements registered a change in inhibitor behavior. These curves were used to calculate the real value of the constant B (Eq. (1)), with which the corrosion-current densities by the R_{p} for each mixture type and inhibitor concentration were calculated [27,28]. The tests were run with the potentiostat, using the following parameters: initial potential = 200 mV more negative than the corrosion potential (E_{corr}); return potential = 900 mV more positive than E_{corr} and final potential = 150 mV more negative than E_{corr}, at 0.28 mV/s.

$$B = \frac{\beta_{\mathrm{a}} \times \beta_{\mathrm{c}}}{2.3 \times (\beta_{\mathrm{a}} + \beta_{\mathrm{c}})}. \tag{1}$$

Ohmic resistance was measured to determine whether it was necessary to correct R_{p} and cyclic curves for IR drop [28]. The values reported are the averages of the values measured in each set of probes according to w/c ratio and inhibitor concentration.

In the polarized samples, chloride-ion content (ASTM D-512-65) at the reinforcement was also determined.

The probes prepared with tap water were sprinkled periodically with tap water for 30 min during the evaluation period (407 days). The probes prepared with lake water (with/without inhibitor) were sprinkled with salt water at 0.3% NaCl for 30 min per day for 115 days. Subsequently, in order to accelerate the process, they were sprayed with NaCl at 3.5% until the 147th day with respect to the preparation of the test probes and, finally, they were placed in a salt chamber with NaCl at 5%, 25°C and 101.3 kPa. This exposure was done for 10.5 h/day, for 500 h. The Q [29] method was used for statistical evaluation of the data for corrosion potentials, corrosion rate, resistivity and IR drop in order to discard non-representative values in the calculation of the median.

3. Discussion of results

3.1. Physical tests

After 28 days, the compressive strength test (ASTM C-39) was applied to the pattern probes (tap water and lake water), the calcium nitrite probes and the 2% calcium nitrite/zinc oxide mixture. This test was carried out on the 3% zinc oxide probes after 69 and 73 days in the case of the 4% zinc oxide probes. This time difference with the zinc oxide probes was due to the retarding effect on setting exerted by zinc oxide, as indicated above [2]. The results for the 2% ZnO probes are not given because they crumbled when they were being prepared for the compressive strength test 28 days after curing.

Fig. 3 shows that the results for all probes (with different w/c ratios and different inhibitor concentrations) were higher than the design strength (w/c = 0.45/310, 0.5/240 and 0.6/160 kg/cm^2), the best behavior being that of 4% calcium nitrite. It should be noted that resistance values grow as concentration of both inhibitors is increased and that strength values at w/c ratio = 0.6 are greater for the zinc oxide probes than for the calcium nitrite. This result has been observed in previous studies [11].

An effective comparison of compressive strength for the different inhibitors tested is very difficult because of curing-time differences for the probes. In the case of the mixture, lower compressive strength was observed at all w/c ratios. Although calcium nitrite is a set accelerator, the retarding action of 2% ZnO prevented the development of adequate compressive strength in the concrete at 28 days' curing. This action was worse (crumbling)

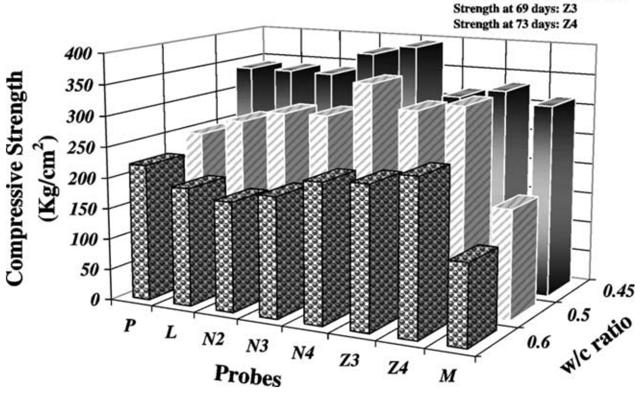

Fig. 3. Compressive strength of probes with different w/c ratios and different inhibitor concentrations.

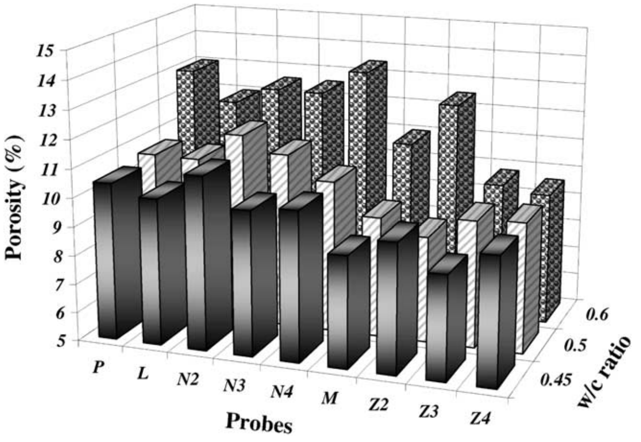

Fig. 4. Porosity of evaluated probes.

when the probes did not contain calcium nitrite, as stated above.

Fig. 4 shows that porosity increases with w/c ratio, except for probes prepared with zinc oxide at 2% and w/c ratio of 0.5, where it decreases when the w/c ratio is increased from 0.45 to 0.5. Porosity decreases up to 3% for probes prepared with zinc oxide and a mixture of inhibitors.

3.2. Electrochemical tests

Studies to date [25] indicate that, for a w/c ratio of 0.6, all steel potentials are active at the end of the evaluation period, except for the tap water probes. However, the time needed for activating the steel is greater in the ZnO than in the $Ca(NO_2)_2$ probes. The lower the w/c ratio, the better the inhibitor behavior, with ZnO being the best. After approximately 300 days' exposure to the marine environment, (w/c = 0.5), the steel was still passive in all probes prepared with ZnO but not with $Ca(NO_2)_2$, where the steel had been activated, regardless of inhibitor content.

This work presents the results for the probes prepared with the best mixture (w/c ratio = 0.45). Fig. 5 shows the best behavior for ZnO and the mixtures. No difference was observed between the tap water and ZnO probes after more than 400 days of exposure to the saline medium.

Initially, very negative steel potentials (active state) were observed during the first days of curing. This is due to different factors, the main ones being the chemical reactions that occur during curing and the lack of oxygen, since the probes are under water [30]. Note the different behavior of the steel in the $Ca(NO_2)_2$ and ZnO probes. With ZnO, the potentials are more negative (indicative of Zn participation in the reactions occurring during this period), and remain for a much longer time because of set retard, which depends on ZnO content.

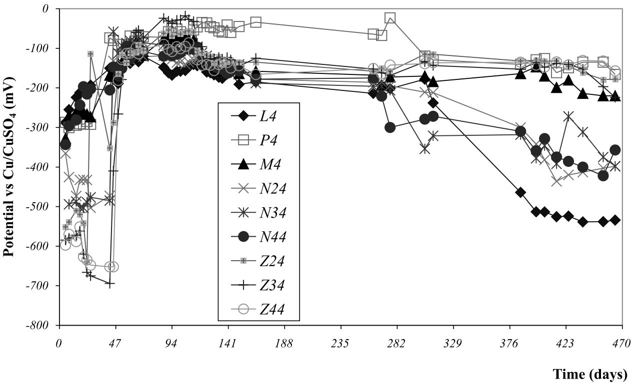

Fig. 5. Average corrosion potential of reinforcing steel in concrete with w/c ratio = 0.45, during the evaluation period.

However, after approximately 50 days, the steel in all the probes becomes passive (potentials more positive than −200 mV vs. $Cu/CuSO_4$ electrode), maintaining its passivity during the evaluation period (more than 400 days). However, the steel in probes without inhibitor (lake water) and with $Ca(NO_2)_2$ showed potentials more negative than −200 mV, after 270 days of exposure, indicative of breaks in the passive film.

This behavior is also evident in Fig. 6, which shows the corrosion-current density variation during the evaluation period. However, the greater steel-corrosion rates were always observed in the ZnO probes, even though they decreased drastically with time, especially for w/c = 0.45 at 3% and 4%, where they have remained constant during the last days of evaluation (300 days). The high corrosion rate is probably due to the presence of Zn on the steel surface, causing a new redox reaction [27,31]. These corrosion rates coincide with those determined for galvanized steel in concrete [32].

Figs. 7–11 show the cyclic curves for the different conditions under evaluation. They show inhibitor behavior under three different conditions: (i) Post-cure (approximately 28 days), (ii) after the steel in some probes started to become activated (approximately 170

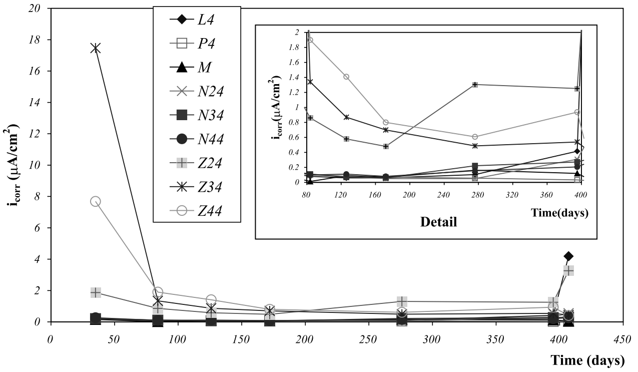

Fig. 6. Variation of average steel corrosion rate of the different inhibitors with w/c ratio = 0.45, during evaluation period.

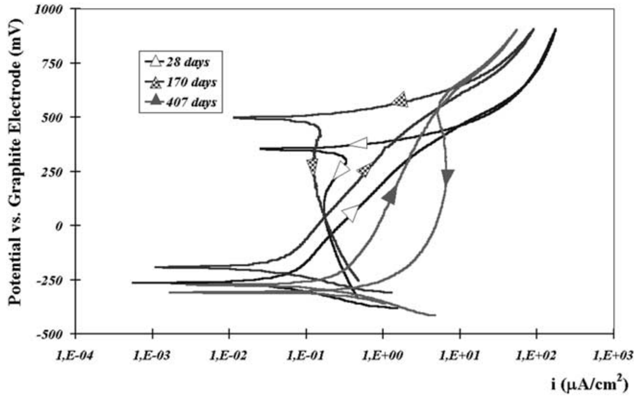

Fig. 7. Potentiodynamic cyclic polarization curves for steel at 0.28 mV/s, at different evaluation times. $Ca(NO_2)_2$ at 4%, w/c ratio = 0.45.

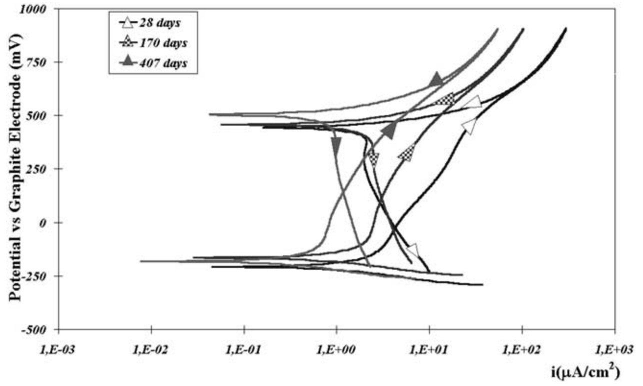

Fig. 8. Potentiodynamic cyclic polarization curves for steel at 0.28 mV/s, at different evaluation times. ZnO at 4%, w/c ratio = 0.45.

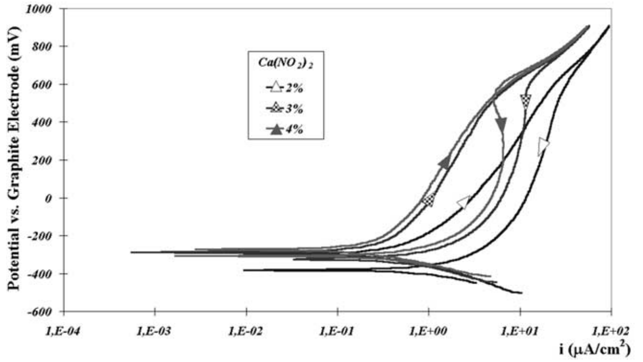

Fig. 9. Potentiodynamic cyclic polarization curves for steel at 0.28 mV/s, in $Ca(NO_2)_2$ as inhibitor, w/c ratio = 0.45, after 407 days' evaluation.

days), and (iii) after 407 days of evaluation. Only the curves for the w/c ratio = 0.45 and 4% inhibitor concentration are presented.

After 28 and 170 days' exposure (Fig. 7), the steel in concrete prepared with $Ca(NO_2)_2$ has a current reversal

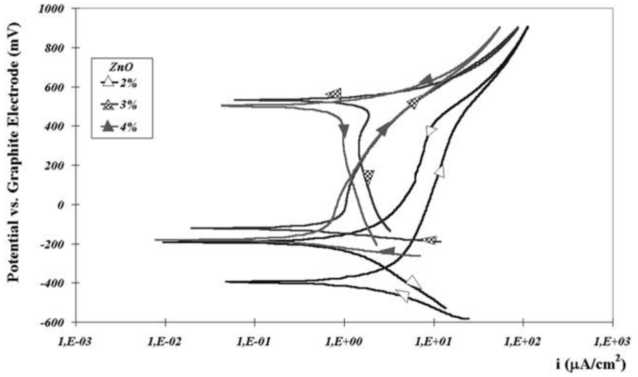

Fig. 10. Potentiodynamic cyclic polarization curves for steel at 0.28 mV/s, in ZnO inhibitor, w/c ratio = 0.45, after 407 days' evaluation.

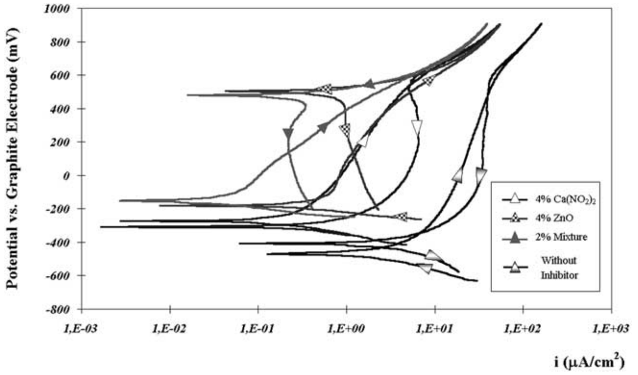

Fig. 11. Comparison between potentiodynamic cyclic curves for steel in different inhibitor mixtures used at w/c ratio = 0.45, after 407 days' evaluation.

in the reverse scan direction at very noble (positive) values of potential. The current reversal occurred at much more active (negative) potential values at 407 days' exposure. This effect is thought indicative of the stability of the passive film [18,33]. The samples for which the current reversal occurred at very noble values had much more stable passive films because, in order to shift the potential in a more active direction, the current shifted to the cathodic direction in order to strip it away. The samples for which the current reversal occurred at more active values had a very unstable passive film or, as is more likely, the case had no passive film at all. Therefore, no stripping current was required to shift the potential in the more active direction. This interpretation is consistent with the known effect of chloride ions in disrupting the passive film.

Fig. 8 shows the behavior of steel when ZnO at 4% is used as corrosion inhibitor in the probes with w/c = 0.45, with similar behavior for $Ca(NO_2)_2$ after 28 and 170 days' exposure to the aggressive medium. However, this inhibitor maintains reinforcement passivity after 407 days' exposure to the saline medium, drastically reducing the passivating current in the same way as in the polarization resistance measurements. This is possibly due to a thickening of the passive film as exposure time elapses.

Figs. 9 and 10 show steel behavior, depending on inhibitor concentration for the same w/c ratio, after 407 days' evaluation. Note that the steel has lost passivity for all $Ca(NO_2)_2$ inhibitor concentrations, with very high currents in the reverse scan. This is not the case for ZnO, where passivity is lost only when concentration is at 2%, where a change from anodic to cathodic current to very negative potentials, close to the corrosion potential, occurs. Note the slight difference between 3% and 4%.

Moreover, the probability of localized corrosion is related to the difference between the repassivation and corrosion potentials. Thus, the higher the difference the lower the probability of crevice corrosion and/or pitting [28]. Fig. 11 shows that this difference is of the order of 700 mV for steel in concrete prepared with ZnO (except for 2%) and the mixture, indicative of a very stable passive film. For $Ca(NO_2)_2$ and the pattern probe (with lake water), this difference is −40 and 60 mV, respectively, with worse behavior for $Ca(NO_2)_2$, where the rebar is already pitted.

The polarization curves for steel in the cylinders containing $Ca(NO_2)_2$ (Figs. 7 and 9), or without inhibitor (Fig. 11) indicate the possibility of pitting or crevice corrosion in the reverse scans. Polarization behavior for steel in the cylinders containing ZnO (Fig. 8) and $Ca(NO_2)_2 + ZnO$ (Fig. 11), displayed non-pitting or crevice-corrosion behavior along with active–passive behavior.

Fig. 11 compares inhibitors with the mixture and the test probe prepared with lake water and exposed to the saline medium. The probes prepared with the mixture show the lowest steel-corrosion rate. Although the corrosion rate for the steel in the ZnO and $Ca(NO_2)_2$ probes is the same, in the latter there is hysteresis behavior in the reverse scan for $Ca(NO_2)_2$, indicating pitting in the sample. As stated above, the potential is more negative.

Table 1 shows the results of the determination of free chloride ions at reinforcement level, after the periods indicated above. Note the effect of ZnO, where concentrations are very low, especially when the w/c ratio is 0.5 and 0.45; the same effect is observed in the mixtures. This may be due to a decrease in concrete porosity and, possibly, to ZnO reaction with the chloride ions, deactivating it.

Table 1
Chloride concentration at reinforcement level (ppm for cement weight)

Probe	A[a]	B[b]	C[c]
P04	327	261	394
P05	346	207	432
P06	383	194	778
M24	1571	1833	784
M25	2214	4419	756
M26	2759	14 090	5186
Z24	2355	2612	2353
Z25	1938	3729	1081
Z26	1842	3683	63 283
Z34	1571	1964	589
Z35	1938	1522	3677
Z36	2148	4143	18 674
Z44	1310	3273	784
Z45	1386	12 870	4543
Z46	2454	13 964	15 562
N24	523	523	5887
N25	484	4845	11 294
N26	844	9348	69 505
N34	327	1833	7456
N35	553	829	14 059
N36	1764	5062	46 165
N44	720	654	8240
N45	484	691	18 277
N46	690	613	42 359
L04	589	3272	18 050
L05	346	4148	10 813
L06	537	3832	51 351

[a] Concentration at end of curing period.
[b] Concentration 170 days after probes were made.
[c] Concentration 400 days after probes were made.

As is well known, ZnO acts as a cathodic inhibitor when used in water since it can precipitate compounds at the cathode because of its high alkalinity in comparison with the anode. However, concrete has high alkalinity, so it is expected that ZnO precipitate compounds both on the cathodic and anodic areas, as well as within the concrete itself. It can be expected [34,35] that ZnO reacts with concrete as follows:

$$ZnO + H_2O + 2OH^- \rightarrow Zn(OH)_4^{2-} \tag{2}$$

$$2Zn(OH)_4^{2-} + Ca^{++} + H_2O \rightarrow Ca(Zn(OH)_3)_2 \cdot 2H_2O + 2OH^- \tag{3}$$

This product $(Ca(Zn(OH)_3)_2 \cdot 2H_2O)$ causes passivation of galvanized steel in concrete. This helps to reduce porosity and maintain the passivity of the steel in the concrete when it is exposed to a medium with high chloride-ion content.

As is well known, calcium nitrite is a typical anodic corrosion inhibitor. It is thought that nitrite ions compete with chloride ions for ferrous ions and react with ferrous ions to produce ferric oxide [10,36].

$$2Fe^{2+} + 2OH^- + 2NO_2^- \rightarrow 2NO + Fe_2O_3 + H_2O \tag{4}$$

$$Fe^{2+} + OH^- + NO_2^- \rightarrow NO + \gamma FeOOH \tag{5}$$

These reactions are much faster than the transport of ferrous ions via chloride-ion complex formation [36]. Thus, nitrite ions aid in the production of a stable passive layer even in the presence of chloride ions, with $\gamma FeOOH$ being the more stable oxide in presence of these ions. However, full protection depends greatly on the concentration of aggressive ions such as the chloride ion. A Cl^-/NO_2^- ratio < 1 was suggested as a precaution against corrosion in reinforced concrete [21,37]. It has been reported that insufficient nitrite concentration increases corrosion activity [38]. So, for $Ca(NO_2)_2$ at 2%, the metal lost passivity even before the 400 days' exposure to the aggressive medium [25]. But when ZnO was added, the steel remained in its passive state, reducing Cl^- content at reinforcement level, which allows $Ca(NO_2)_2$ to act efficiently on the reinforcement, passivating it. To date, there is no exact knowledge of how ZnO action causes reinforcement passivation. It is currently under investigation at CEC [39].

4. Conclusions

1. Chloride diffusion and, therefore, corrosion rate, is controlled by reducing the w/c ratio to 0.45, regardless of calcium nitrite content.
2. The use of ZnO reduces concrete porosity and chloride content at rebar level.
3. After the exposure period (≈500 days), the potential values (>-200 mV vs. $Cu/CuSO_4$) and cyclic curves of the steel in the probes with ZnO show passivation, even though corrosion rates are high ($>0.1\ \mu A/cm^2$).
4. When ZnO is used, an appreciable change in corrosion rate is observed when the inhibitor concentration is changed from 2% to 3%.
5. After approximately 500 days' exposure to the saline medium, all the probes prepared with $Ca(NO_2)_2$ showed breaks in the passive film on the reinforcement.
6. The $ZnO/Ca(NO_2)_2$ mixture at 2% showed the best results throughout the study period.

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