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EFFECTIVENESS OF CNI IN HIGH-PERFORMANCE CONCRETE

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ABSTRACT

The effectiveness of calcium nitrite based corrosion inhibitor as a prevention method of steel reinforcing bars embedded in high performance concrete slabs was investigated. A 3^3 full factorial design was developed considering CNI dosage, water to cement ratio and fly ash percent as factors. The response was the corrosion current density. Small-scale concrete slabs containing steel reinforcement were cast in concrete with a cover depth of 20 mm. The slabs were exposed to a natural marine environment during six years with two cycles of wetting and drying per day at the Fundy Bay, Maine, U. S. A. The specimens were also visually inspected on regular basis and the surface damage was recorded. It was found that for most of the cases the use of CNI inhibitor was beneficial in concrete.

Keywords: Calcium nitrite, concrete cracking, corrosion, fly ash, corrosion current density.

RESUMEN

En el presente estudio se evaluó la efectividad de un inhibidor de nitrito de calcio como método para prevenir la corropsión del acero de refuerzo en losas de concreto. Para tal efecto se diseñó un experimento factorial completo 3^3, con dosis de CNI, rel. agua/cemento y porcentaje de ceniza volante como factores. La variable respuesta fue la densidad de corrosión. Se colaron losas pequeñas que contenían acero de refuerzo con un espesor de recubrimiento de 20 mm. Se expusieron las losas a un ambiente marino natural durante seis años con ciclos de humedecimiento y secado en la Bahía de Fundy, Maine, Estados Unidos. Se inspeccionaron los especímenes regularmente y se registró el daño en la superficie. Los resultados indican que para la mayoría de los casos el uso de inhibidor en concreto a base de CNI fue benéfico.

Palabras clave: Nitrito de calcio, agrietamiento en concreto, corrosión, ceniza volante, densidad de corrosión.

INTRODUCTION

Chloride-induced corrosion of steel reinforcement is one of the most serious problems in reinforced concrete structures. Several methods have been proposed to solve the problem, namely: epoxy coatings, a low permeability concrete, use of supplementary materials and corrosion inhibitors. Each method alone provides insufficient protection to the steel reinforcement due to the complex nature of corrosion, and seems to be the combination of two or more methods the appropriate approach to alleviating this problem. Nitrites are anodic inhibitors that apparently aid the formation of a stable passive layer on the steel reinforcement even in the presence of chloride ions [1,2,3,4]. However, full protection depends greatly on the concentration of aggressive ions such as the chloride ions[2].

The literature reports that CNI was effective at an addition amount of 25 L/m^3 in concrete of w/c of 0.6 and 0.4 but the addition of 11 L/m^3 in 0.25 w/c ratio concrete it was only marginally effective[6]. However, in another study CNI was only effective in delaying corrosion but not effective after the initiation of corrosion[7]. More research studies show that CNI inhibitor was incapable of re-establishing passivity with increasing chloride concentration after the breakdown of the protective film[2, 8]. The combination of good quality concrete (w/c=0.29 or 0.37) and the use of CNI at an addition rate of 12.5 L/m^3 plus the use of 20% of fly ash appears to be the desirable approach to reduce the effect of chloride induced corrosion of steel reinforcement[9]. The addition of 12.5 L/m^3 CNI decreases corrosion cracking in concrete, but a dosage higher than 12.5 l/m^3 does not show significant improvement[5]. Even for uncracked concrete in a 0.45 w/c ratio, CNI failed to prevent the development of corrosion[10].

In the presente work, four factors affecting corrosion of reinforced concrete were evaluated, namely, water to cement ratio, fly ash content and calcium nitrite-based corrosion inhibitor (CNI) addition rates.

EXPERIMENTAL

Design of the experiment and materials

To evaluate the effectiveness of Calcium Nitrite based corrosion inhibitor (CNI) in concrete, the combination of 0.29, 0.37 and 0.45 water to cement ratio concrete containing 0, 20 and 40% fly ash and three different amounts were studied in concrete specimens exposed to a natural marine environment during six years. The materials used in the test program consisted of the following:

Portland Cement. CSA Type 10L-SF low alkali Portland cement which incorporated 8.2% silica fume cement replacement was used for all the mixtures. Its chemical and physical analysis is given in Table 1.

Fly Ash. The fly ash used belongs to Type F in ASTM classification[11], the physical and chemical characteristics are given in Table 2.

Aggregates. Coarse aggregate used was crushed limestone with a maximum size 12.5 mm and a relative density of 2.69. Fine aggregate used was a natural river sand with a fineness modulus of 2.65 and a relative density of 2.62.

Chemical admixtures. The chemical admixtures used were an air entraining admixture meeting ASTM C 260, a set retarder meeting ASTM C 494 and a High Range Water Reducer meeting ASTM C 494, Type F Superplasticizer[11].

Calcium Nitrite Based Corrosion Inhibitor. The commercial calcium nitrite based corrosion inhibitor used in this study contains a minimum of 30% calcium nitrite.

Simulated salt water. The solution was prepared as recommended by the ASTM D 1141-80 Standards[11].

Table 1. Chemical and Physical Analysis of Cement

Chemical Composition	Test Result	Physical Analysis	Test Result
Silica (SiO_2)	26.7 %	Fineness 45mm sieve	94.3 % passing
Alumina (Al_2O_3)	4.0 %	Blaine (Spec. Surf)	555m^2/kg
Iron Oxide (Fe_2O_3)	2.9 %	Vicat Setting Time	125 minutes
Calcium Oxide, Total (TCaO)	59.6 %	Autoclave Expansion	0%
Magnesium Oxide (MgO)	0.9 %	Compressive Strength at 3 days	26.0 MPa
Sulphur Trioxide	2.7 %	Compressive Strength at 7 days	35.1 MPa
Loss of ingnition	1.7 %	Compressive Strength at 28 days	55.1 MPa
Calcium Oxide, Free (FCaO)	1.5 %	% of Silica Fume	8.2 %
Equivalent Alkali (as Na_2O)	0.46 %		
Potential Compounds			
C_3A	5.7%		

Table 2. Chemical and Physical Analysis of Fly Ash

Physical analysis	Test Result	Specification Limits for Class F Fly Ash ASTM C618-94	CSA A23.5-M86
Strength Activity Index %			
with Portland Cement at 7 days	81.3	Min. % of control, 75	Min. % of control,68
at 28 days	87.1	Min. % of control, 75	Min. % of control, 75
Fineness			
% retained on 45 mm sieve	13.2	Max 34%	Max. 34%
Soundness, Autoclave			
Expansion or contraction, %	0.03	Max. 0.8%	Max 0.8%
Water Requirement			
% of control	95.0	Max. 105%	N/A
Chemical Requirements			
SiO2 + AI2O3 + FeO3, %	81.6	70.0 %	N/A
(35.0 + 15.2 +31.4)			
SO3, %	2.01	5.0%	Max. 5%
Moisture Content, %	0.15	3.0%	Max. 3%
Loss of Ignition, %	2.03	6.0%	Max. 12%
Specific Gravity	2.5	---	---
Carbon, %	0.45	---	---
Total Alkalies, %	1.70	---	---
Soluble Alkalies, %	0.138	---	---

Mixture proportions and specimen preparation

Twenty-seven concrete mixtures were prepared in total (Table 3) and two slabs were cast for each mixture proportion, the nominal dimensions of the concrete slabs were 55x230x300 mm. The thickness and width of the specimens were adjusted to provide a cover of 20 ± 2 mm to accelerate the corrosion process. Tests of the properties of the concrete in its fresh state such as slump, air content and density were performed and the results were also recorded in Table 3.
Two 15 mm of diameter black bars were embedded in each concrete slab. The target slump was 100 mm and an air content of 7%.

Table 3. Mixture Proportions (per m^3)

Mix #	Fly Ash kg	Cement +SF kg	CA kg	FA kg	Water kg	AEA mL	HRWR mL	Set Ret. mL	CNI mL	w/c	Air %	Slump mm.	Unit Weight kg/m3	f'c (28 days)
1	0	544	1029	664	154	587	2844	1087	0	0.28	4	165	2415	72
2	0	544	1029	664	155	1413	2844	1087	12500	0.29	6	159	2380	82
3	0	544	1029	664	155	1859	2844	1087	25000	0.29	5	197	2362	78
4	87	422	992	646	148	1049	2202	1052	0	0.29	6	178	2330	62
5	87	422	992	646	148	1498	1858	1052	12500	0.29	7	188	2294	67
6	87	422	992	646	149	1798	1783	1052	25000	0.29	7	166	2262	67
7	177	317	987	650	145	1048	841	1051	0	0.29	8	115	2256	42
8	177	317	987	650	145	1198	939	1051	12500	0.29	8	130	2270	54
9	177	317	987	650	145	1048	946	1051	25000	0.29	7	159	2277	51
10	0	441	997	702	165	591	1491	1037	0	0.37	7	146	2288	54
11	0	441	997	702	165	650	1241	1037	12500	0.37	6	172	2298	62
12	0	441	997	702	165	591	1063	1037	25000	0.37	6	146	2309	65
13	73	351	986	694	158	803	840	513	0	0.37	8	108	2241	43
14	73	351	986	694	158	657	942	513	12500	0.37	7	127	2263	46
15	73	351	986	694	158	730	752	513	25000	0.37	8	134	2262	50
16	150	268	993	699	156	846	941	0	0	0.37	8	121	2248	31
17	150	268	993	699	156	706	676	0	12500	0.37	8	121	2270	38
18	150	268	993	699	155	691	368	0	25000	0.37	8	146	2256	40
19	0	371	958	691	168	610	0	995	0	0.45	8	121	2174	34
20	0	371	958	692	167	539	0	995	12500	0.45	7	127	2163	39
21	0	371	958	692	167	425	0	995	25000	0.45	8	146	2202	45
22	63	300	963	708	165	428	274	390	0	0.45	6	108	2199	33
23	63	300	963	708	164	428	0	390	12500	0.45	8	140	2188	31
24	63	300	963	749	164	214	0	390	25000	0.45	8	153	2227	42
25	132	236	992	731	167	324	397	0	0	0.45	7	105	2224	26
26	132	236	995	728	166	397	0	0	12500	0.45	7	134	2234	27
27	132	236	995	728	166	162	0	0	25000	0.45	6	185	2284	32

Notes:
CA : Coarse Aggregate, FA: Fine Aggregate, AEA : Air Entraining Agent, HRWR : High Range Water Reducer, CNI : Calcium Nitrite Based Corrosion Inhibitor

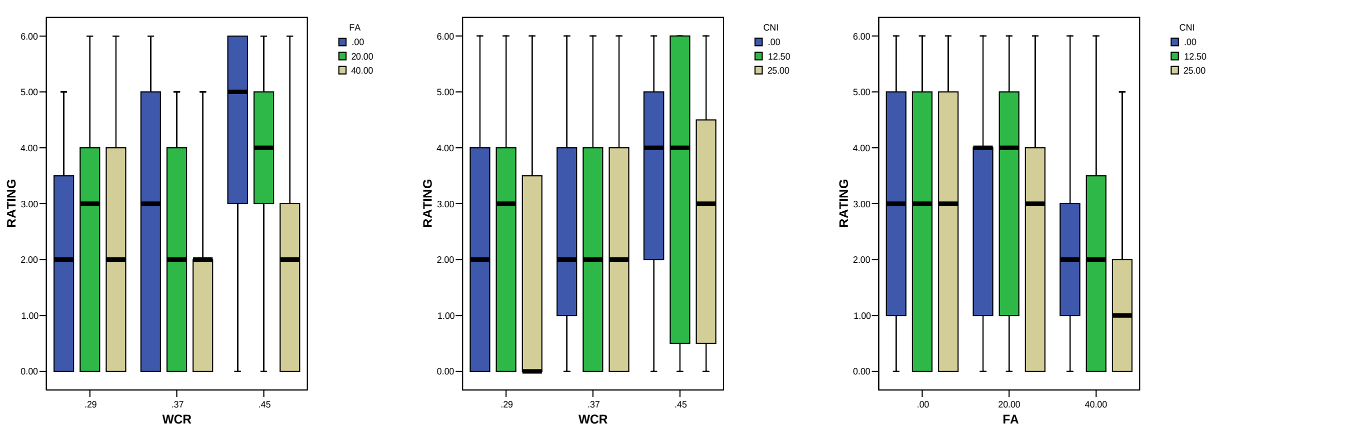
Experimental procedures

To evaluate the influence of seawater on corrosion of reinforcing bars embedded in the concrete specimens, the specimens were placed at the Corps of Engineers testing facility located in Maine, U.S.A. The corrosion current density of the reinforcing steel bars was monitored yearly during six years by using linear polarization resistance technique, LPR. The surface of the concrete slabs were also visually inspected on a regular basis and the existence of stains, number of cracks caused by corrosion and concrete deterioration, if any, were noted throughout the testing program. For evaluating the effects of w/cm, CNI, and fly ash and their possible interactions on corrosion- induced cracks, the number of such cracks for each specimen was quantified and arranged in boxplots.

RESULTS

Visual inspection

Due to the great variability of results for most of the treatments, it was decided to compare the medians of the numbers of cracks between specimens by using box-plots. The results indicate that when 20% fly ash is added to the mixtures, corrosion-induced cracking is decreased for most of the cases (fig. 1a). For 40% fly ash, the number of cracks observed was less or stayed the same as the control. Regarding the inhibitor, a dosage of 25 L/m^3 of CNI did not showed any improvement in preventing cracking. However, 25 L/m^3 decreased cracking in 0.29 and 0.45 w/cm ratio concretes (fig. 1b). Figure 1c shows the CNI-fly ash interaction, where it is evident tha CNI is more effective in concrete containing fly ash. The present findings have to be corroborated with LPR measurements in the next section.



a) Effect of fly ash on w/cm b) Effect of CNI on w/cm c) Effect of CNI on FA

Figure 1. Results of visual inspection

LPR test results

Most of the Icorr values ranged between 0.1 and 1.0 μA/cm^2 which suggests low and moderate corrosion rate[12], the exception were those for 0.45 w/cm ratios where readings as high as 10 μA/cm^2 were registered, indicating severe corrosion.

It was observed a beneficial effect of 20% fly ash only for 0.29 w/cm ratio concrete (Fig. 2, f), but this effect was more evident when fly ash was increased to 40% (Fig. 2, g, h, i).

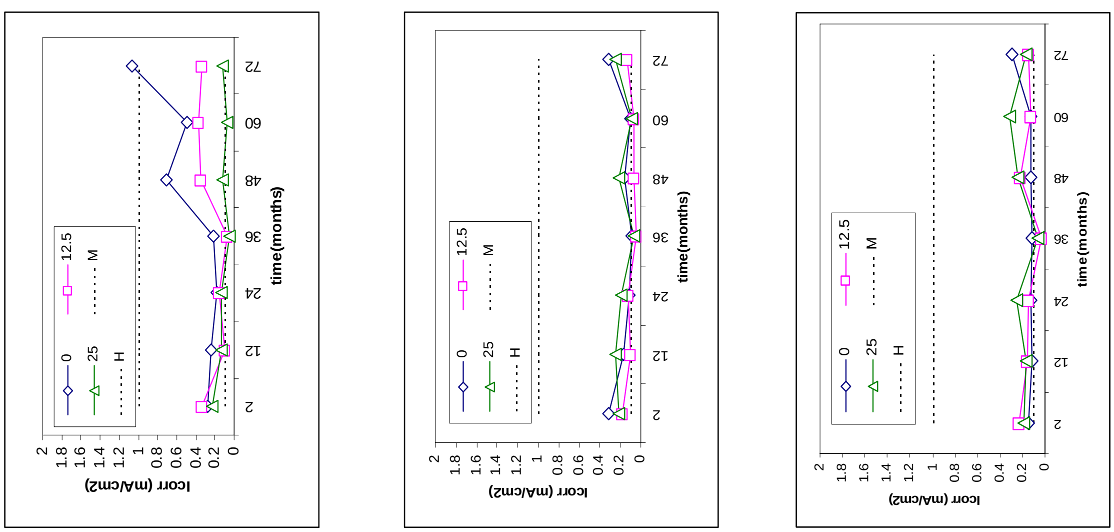
CNI in a dosage of 12.5 L/m^3 had a beneficial effect decreasing corrosion for most of the concretes, and 25 L/m^3 showed better performance (Fig. 2, a, b, c). This corroborates that a high dosage of CNI is beneficial and necessary to maintain the passive layer on the steel reinforcement.

The combination of CNI and fly ash was beneficial for all the concretes studied. This is clearly in opposition to some findings reported in the literature[13,14]. The present study shows that in 0.29 and 0.37 w/cm ratios CNI and fly ash together contributed to keep very low Icorr readings. However, for the 0.45 w/cm ratio concrete, this combination, even though was better than the control, was not enough to prevent corrosion unless a large volume of fly ash was added to the mixture. In summary, the results strength the argument that neither fly ash nor CNI can be used separately to prevent corrosion in reinforced concrete exposed to an aggressive media, such as a marine environment.

Fly ash

0% 20% 40%

0.29 w/c



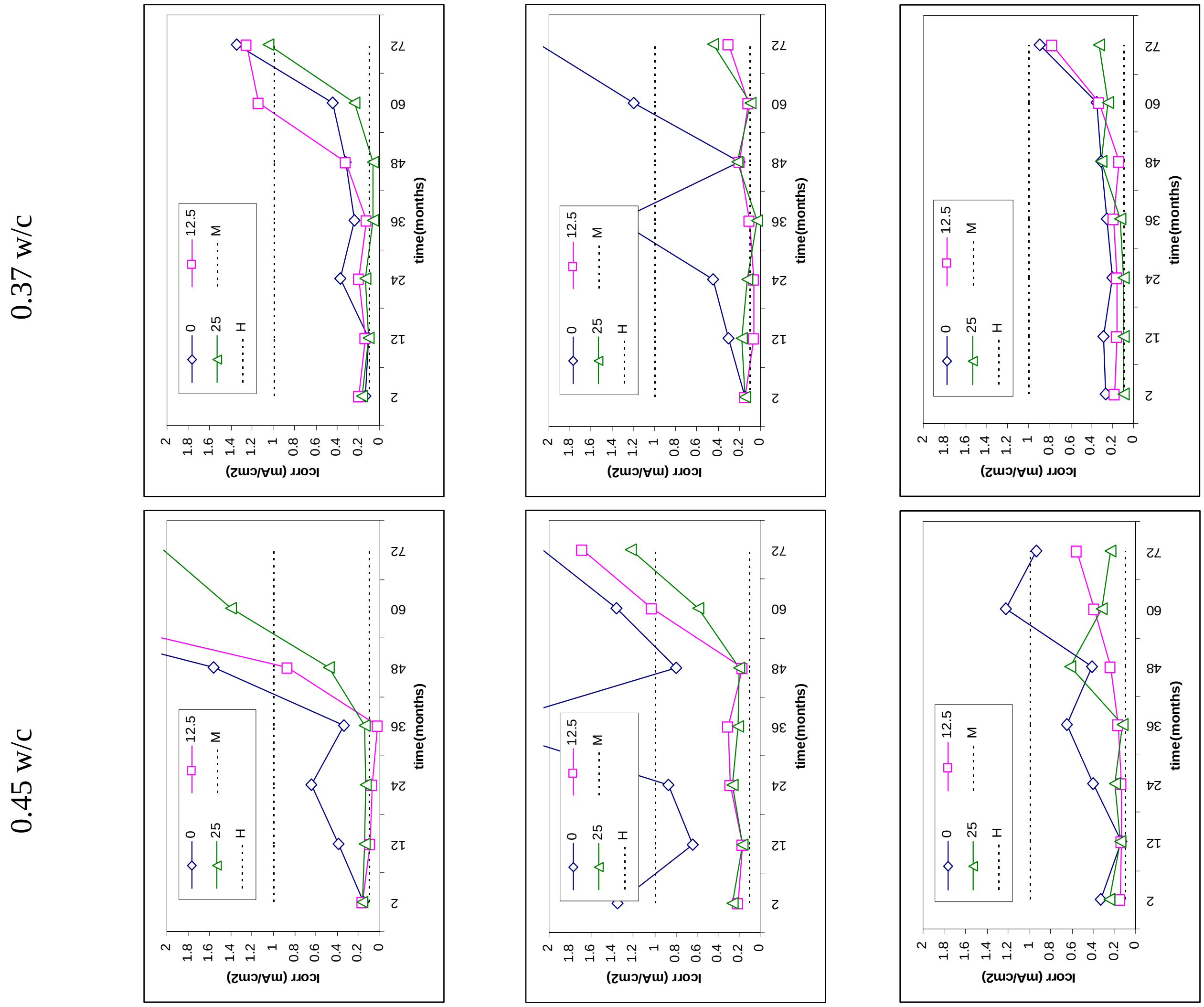


Figure 2. LPR results (μA/cm^2).

CONCLUSIONS

Based on the analysis of the results the following conclusions can be drawn:

- It was found that, under the studied conditions, there is a good correlation between results of the visual inspection analysis and corrosion current density obtained from LPR testing.
- Results also indicate that the w/c ratio has a marked influence on the Icorr results; a higher corrosion activity was registered for higher w/c ratio specimens.
- The addition of fly ash has also an important beneficial effect decreasing Icorr.
- Finally, results showed that the combination of fly ash and CNI is not detrimental; conversely, specimens containing such combination experienced low corrosion activity.

Continuing research

More research is needed on involving full-scale structural members subjected to marine exposure. The results obtained from this research should be used in planning these long-term experiments.

Acknowledgments

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