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Influence of calcium nitrite inhibitor and crack width on corrosion of steel in high performance concrete subjected to a simulated marine environment

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Abstract

The effects of calcium nitrite based corrosion inhibitor (CNI) and crack width on the corrosion process of steel reinforcing bars in high performance concrete were investigated. A 3^4 full factorial design was developed considering water to cement ratio, fly ash percent, CNI and cracked condition as factors. The response was the corrosion current density measured using the linear polarization resistance technique. Small-scale concrete slabs containing steel reinforcement were cast in concrete with a cover depth of 20 mm. The slabs were subjected to a simulated marine environment with two cycles of wetting and drying per day. The specimens were also visually inspected on a regular basis. It was found that CNI alone, in general, has no effect in decreasing corrosion, and that the crack condition of the specimens strongly affects the corrosion process. A significant effect of crack width on corrosion was also found. Furthermore, non-detrimental effect of CNI on corrosion of specimens containing fly ash was detected.

Keywords: Calcium nitrite corrosion inhibitor; Cracked concrete; Fly ash; High performance concrete; Water to cement ratio

1. Introduction

Chloride-induced corrosion of steel bars is one of the most serious problems in reinforced concrete structures. Every year, several millions of dollars are spent to repair concrete structures damaged by corrosion [1–3]. Several methods have been proposed to prevent corrosion of steel in concrete, including, corrosion inhibitors, epoxy-coated reinforcing bars, galvanized steel bars with a sacrificial zinc layer, and low permeability concrete with pozzolanic admixtures (high performance concrete). Each method alone provides insufficient protection to the steel reinforcement due to the complex nature of corrosion, and it is the combination of two or more methods which seems to be the appropriate approach to alleviating this problem.

In view of this, four factors affecting corrosion were investigated, namely, water to cement ratio, fly ash content, corrosion inhibitor (CNI) addition rates and the degree of cracking of the concrete. A 3^4 full factorial design was developed considering the effect of these factors. The response was the corrosion current density measured using the Linear Polarization Resistance technique of small scale concrete slabs containing steel reinforcement, which were subjected to a simulated marine environment for one year.

2. Effect of water to cement ratio (w/c ratio)

The water to cement ratio is an important parameter affecting the properties of both fresh and hardened concrete. In fresh concrete, a large amount of cement decreases workability. In the same way, a small amount of cement causes problems when placing concrete in the forms due to the lack of enough fine particles in the mixture.

The water to cement ratio is one of the most important parameters affecting the long-term properties of concrete. For cement pastes hydrated to the same degree, the permeability is lower the higher the cement content of the paste, i.e. the lower the water to cement ratio [4]. Also it is widely known that the permeability of reinforced concrete is an important factor limiting the

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ingress of chlorides, which promote the corrosion of the reinforcing bars [5].

A low w/c ratio not only will slow the diffusion of chlorides, carbon dioxide, oxygen and other aggressive agents but also will increase the strength of concrete, extending the time before corrosion induced stresses cause cracking [6].

The value of the w/c ratio is relevant to many aspects of durability; however, it has also been suggested that the w/c ratio alone does not determine the durability or even the permeability of the concrete [7]. According to this, the w/c ratio is not an indicator of durability; it is its interaction with some other factors such as supplementary cementing materials and chemical admixtures that need to be investigated.

3. Effect of fly ash

Fly ash, a by-product of coal combustion, is widely used in concrete because of several beneficial effects it has on the properties of both fresh and hardened concrete. The slower reaction of fly ash as compared to Portland cement limits the heat of hydration and temperature rise in fresh concrete [8].

In hardened concrete, fly ash decreases the permeability of concrete [9], consequently, the chloride-ion penetration of the concrete is minimized and its resistivity increased. This improvement in the concrete's characteristics prevents the embedded reinforcing bars in the concrete to be reached by aggressive agents, thereby lowering the propensity for corrosion to occur.

There are many other beneficial effects on the properties of concrete by using fly ash. As summarized by Joshi [10], fly ash provides cost savings, improved workability and pumpability, better surface finishing, lower heat of hydration, improved long term and ultimate resistance, reduced permeability, improved sulfate resistance and prevents corrosion of the reinforcement.

The effect of fly ash on the properties of concrete has been studied by many researchers, for instance, Thomas and Banforth modeled the chloride diffusion in concrete containing fly ash and found that the rate of reduction of diffusivity is far greater for concrete containing fly ash than for ordinary Portland cement concrete [11]. They concluded from their work that the use of fly ash considerably increases the service life of structures exposed to chloride environments.

Even a high volume of fly ash in concrete has been reported to provide excellent resistance to chloride-ion penetration [12]. These findings are of considerable importance from the standpoint of durability of structures including control of corrosion of reinforcing steel exposed to a chloride laden environment.

Fly ash in combination with other supplementary cementing materials and superplasticizers can lead to economical high-performance concrete with enhanced durability as suggested by Malhotra [13]. Based on this research, the use of fly ash in concrete has proven highly beneficial; however, with the addition of so many other components in the mixture, the final properties of concrete are not always known, and it is necessary to focus on research studying the combined effect of fly ash with chemical admixtures such as corrosion inhibitors.

4. Effect of calcium nitrite based corrosion inhibitor

Corrosion inhibitors are chemical admixtures, which are added to concrete to protect the steel reinforcing bars from corrosion and in some cases to improve the concrete properties such as permeability. Corrosion inhibitors have been used successfully in some applications like steel pipelines; however, their use in concrete is recent and more limited. Due to the discrepancy in results obtained by some researchers, there is a natural reluctance to use them because they cannot be changed if at a later date they are found to have a negative effect on the reinforcement corrosion process or some others properties of concrete.

Corrosion inhibitors are promoted as an alternate method for preventing and/or delaying corrosion of steel in concrete, however, as suggested by Hansson et al. [14], the mechanism of inhibition must be understood to ensure their proper use. Calcium nitrite is an anodic inhibitor, which apparently elevates the chloride corrosion initiation concentration and delays the onset of corrosion as reported by Berke [15]. It protects the steel reinforcement from corrosion by stabilizing the passive protective layer on the metal surface. It is also suggested that CNI significantly improves the corrosion resistance of steel in concrete with w/c values under 0.5 [16].

Calcium nitrite has been reported to be also compatible with silica fume, and it is suggested that it provides protection to the reinforcing steel bars in the presence of chlorides [17]. Similar results have been reported by other researchers [18].

On the contrary, some researchers have reported detrimental effects of calcium nitrite on the properties of concrete and that it has apparently poor performance in preventing corrosion of steel reinforcing bars. For example, Li et al., suggested that the addition of CNI into high-performance concrete in combination with fly ash weakens the concrete resistance to chloride diffusion, and the compressive strength of mixtures containing CNI is reduced in comparison with that of the control mixture [19]. However, the use of CNI was found to have a non-detrimental effect on the 28-day compressive strength of concrete [20]. Li et al., also reported an increased micropore volume in the concrete mixture and that CNI lowers the resistance to sulfate attack of concrete when CNI is added [21,22]. Nmai and MacDonald reported that CNI seems to be ineffective at reducing corrosion, unless a large amount is added to the mixture [23].

5. Effect of crack width

In concrete, microcracks already exist due to its unstable condition as a composite material. Some other cracks develop when concrete is exposed to environmental gradients or service loads. Therefore, studies on cracked reinforced concrete are essential.

In the past, some researchers have attempted to determine the effect of cracks on the generation and development of corrosion in reinforced concrete. The problem to identify whether cracks cause corrosion or corrosion causes cracking of concrete has been discussed by Metha and Gerwick [24]. They suggested that crack width does not play an important role for significant corrosion to occur, but that the total area covered by cracks next to the surface of the steel does. However, in their study only w/c ratios higher than 0.4 were considered.

According to Sagues and Kranc [25], cracks in concrete may cause localized chloride ingress and the initiation of rebar corrosion. Early cracks due to service loading in reinforced concrete structural members exposed to an aggressive environment may open a direct path to the rebar and thus provide ideal conditions for the corrosion process to start.

Crack width has also been reported to have a significant effect on corrosion of low w/c concrete [26], however, this study was performed considering only two w/c ratios and was conducted over a very short period of time.

In another study [27] it was reported that crack width of less than 0.5 mm affects the development of corrosion, but its width has not a significant influence at later stages in the corrosion process. However, the same authors concluded later that the development of corrosion is not influenced by the crack width or by the crack itself [28].

After an extensive review of the influence of cracking on the deterioration of concrete, Jacobsen et al., concluded that crack widths smaller that 0.4 mm do not adversely affect corrosion of steel as compared to steel in uncracked concrete [29], and some other factors such as environment, quality and thickness of the cover are more important. They also pointed out that most of the studies considered have been carried out on conventional concretes and more information about the effect of cracking on high performance concrete is necessary.

Peter SchieBl and Michael Raupach [30] performed an extensive review on the influence of crack width on chloride-induced corrosion. They concluded that corrosion is only slightly affected by the presence of cracks and corrosion protection must be assured by the use of adequate quality concrete and suitable cover depth. However, CNI has been reported to be effective in high and low w/c ratio concrete in cracked reinforced concrete when subjected to short and extended periods of simulated marine exposure [31].

The use of corrosion inhibitors in cracked concrete tends to "reinforce" the cathodic region in the uncracked area, thus raising the "throwing power" of a corrosion macrocell formed in the cracked concrete has been reported by others [32–34]. In recent studies in cracked concrete, CNI was found to be relatively ineffective in preventing corrosion of small slabs subjected to a natural marine environment [35]. Consequently, more work in this area is necessary to provide additional information about the influence of CNI, crack width and the possible interaction between them in the development of corrosion of reinforcing bars in concrete.

6. Experimental

6.1. Design of the experiment

Previous studies have shown that steel embedded in cracked low water to cement ratio concrete gives poor performance when subjected to marine exposure conditions [32,33,35]. This kind of concrete has in general low permeability, but due to the cracks the chlorides are in direct contact with the reinforcement in the crack area, promoting the development of pitting corrosion.

To evaluate this, 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 of CNI were studied in precracked concrete specimens subjected to simulated and natural marine environments (see Table 1). This study considers only the specimens subjected to the simulated environment and the results from the ones subjected to the natural marine environment will be reported later.

7. Materials

The materials used in the test program consisted of the following:

Table 1
Selection of the independent variables or factors to be investigated in the experiment

Factors (k)	No. of levels	Description
Crack width, A	3	0, 0.25 and 0.5 mm
Water/cement ratio, B	3	0.29, 0.37 and 0.45
Fly ash content, C	3	0%, 20% and 40%
Corrosion inhibitor percentage, D	3	0, 12.5 and 25 L/m^3

Table 2
Chemical and physical analysis of cement

Chemical composition	Test result
Silica (SiO_2)	26.7%
Alumina (Al_2O_3)	4.0%
Iron oxide (Fe_2O_3)	2.9%
Calcium oxide, total (TCaO)	59.6%
Magnesium oxide (MgO)	0.9%
Sulphur trioxide	2.7%
Loss of ignition	1.7%
Calcium oxide, free (FCaO)	1.5%
Equivalent alkali (as Na2O)	0.46%
Potential compounds	
C_3A	5.7%
Physical analysis	
Fineness 45 mm sieve	94.3% passing
Blaine (Spec. Surf)	555 m^2/kg
Vicat setting time	125 min
Autoclave expansion	0%
Compressive strength at 3 days	26.0 MPa
Compressive strength at 7 days	35.1 MPa
Compressive strength at 28 days	55.1 MPa
% of silica fume	8.2%

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 2.

Fly ash. The fly ash used belongs to Type F in the ASTM classification [36], the physical and chemical characteristics are given in Table 3.

Aggregates. Coarse aggregate used was crushed limestone with a maximum size of 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 [36].

Calcium nitrite based corrosion inhibitor. The commercial calcium nitrite based corrosion inhibitor used in this study contains a minimum of 30% calcium nitrite. According to the manufacturer this anodic inhibitor prevents corrosion by chemically reacting with the reinforcing steel. Then, a barrier is formed which prevents chlorides from reaching the steel bars.

Simulated salt water. The solution was prepared as recommended by the ASTM D 1141-80 Standards [36].

8. Mixture proportions and specimen preparation

The concrete mixtures were prepared by adding sand to the mixer followed by one liter of water containing the air entrainment agent. A mixing period of two minutes to evenly distribute the admixture was followed by the incorporation of the coarse aggregate. Silica fume cement was then added to the mixture followed by the fly ash. The additional water containing the set retarder was then added. CNI was incorporated in the mixture and finally, the superplasticizer was added. After a further two minutes mixing period, tests for slump, air content, and density were performed and the results recorded in Table 4.

This work is part of a much larger program that evaluates the influence of fly ash and CNI on the corrosion rate of cracked and uncracked reinforced concrete in simulated and natural marine environment. In the near future, the results of corrosion in the natural

Table 3
Chemical and physical analysis of fly ash

	Test result	Specification limits for class F fly ash	
		ASTM C618-94	CSA A23.5-M86
Physical analysis			
Strength activity index%			
With Portland cement at 7 days	81.3	Min. % of control, 75	Min. % of control, 68
With Portland cement 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			
$SiO_2 + AI_2O_3 + FeO_3$, % (35.0 + 15.2 + 31.4)	81.6	70.0%	N/A
SO_3, %	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	2.86	–	–
Carbon, %	0.45	–	–
Total alkalies, %	1.70	–	–
Soluble alkalies, %	0.138	–	–

Table 4
Mixture proportions (kg/m^3)

Mix-ture number	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/m^3)
1-1	0	544	1029	664	154	554	2844	1087	0	0.28	4	114	2411
1-2	0	544	1029	664	154	620	2844	1087	0	0.28	3	216	2418
2-1	0	544	1029	664	155	1413	2844	1087	12500	0.29	8	178	2348
2-2	0	544	1029	664	155	1413	2844	1087	12500	0.29	3	140	2411
3-1	0	544	1029	664	155	1859	2844	1087	25000	0.29	6	191	2312
3-2	0	544	1029	664	155	1859	2844	1087	25000	0.29	3	203	2411
4-1	87	422	992	646	148	1049	2202	1052	0	0.29	5	229	2369
4-2	87	422	992	646	148	1049	2202	1052	0	0.29	7	127	2291
5-1	87	422	992	646	148	1498	2202	1052	12500	0.29	6	229	2326
5-2	87	422	992	646	148	1498	1513	1052	12500	0.29	8	146	2262
6-1	87	422	992	646	149	1798	2202	1052	25000	0.29	6	229	2262
6-2	87	422	992	646	148	1798	1363	1052	25000	0.29	8	102	2262
7-1	177	317	987	650	145	1048	841	1051	0	0.29	8	127	2241
7-2	177	317	987	650	145	1048	841	1051	0	0.29	7	102	2270
8-1	177	317	987	650	145	1198	886	1051	12500	0.29	8	127	2262
8-2	177	317	987	650	145	1198	991	1051	12500	0.29	7	133	2277
9-1	177	317	987	650	145	1048	991	1051	25000	0.29	7	178	2262
9-2	177	317	987	650	145	1048	901	1051	25000	0.29	7	140	2291
10-1	0	441	997	702	164	591	1181	1037	0	0.37	8	152	2270
10-2	0	441	997	702	165	591	1801	1037	0	0.37	6	140	2305
11-1	0	441	997	702	164	561	1004	1037	12500	0.37	6	140	2291
11-2	0	441	997	702	165	738	1477	1037	12500	0.37	6	203	2305
12-1	0	441	997	702	164	591	886	1037	25000	0.37	6	152	2291
12-2	0	441	997	702	165	591	1240	1037	25000	0.37	6	140	2326
13-1	73	351	985	694	158	876	1051	1025	0	0.37	8	114	2255
13-2	73	351	986	694	158	730	628	1025	0	0.37	8	102	2227
14-1	73	351	985	694	158	730	920	1025	12500	0.37	8	152	2220
14-2	73	351	986	694	158	584	963	0	12500	0.37	6	102	2305
15-1	73	351	985	694	157	584	817	1025	25000	0.37	7	140	2262
15-2	73	351	986	694	158	876	686	0	25000	0.37	8	127	2262
16-1	150	268	993	699	155	882	618	0	0	0.37	8	114	2248
16-2	150	268	993	699	156	809	1264	0	0	0.37	8	127	2248
17-1	150	268	993	699	156	735	676	0	12500	0.37	8	114	2255
17-2	150	268	993	699	155	676	676	0	12500	0.37	7	127	2284
18-1	150	268	993	699	155	735	0	0	25000	0.37	8	140	2227
18-2	150	268	993	699	155	647	735	0	25000	0.37	7	152	2284
19-1	0	371	957	703	169	709	0	995	0	0.45	8	114	2191
19-2	0	371	958	678	166	510	0	995	0	0.45	8	127	2156
20-1	0	371	957	705	167	567	0	995	12500	0.45	6	127	2156
20-2	0	371	958	678	166	510	0	995	12500	0.45	8	127	2170
21-1	0	371	957	705	167	425	0	995	25000	0.45	7	127	2213
21-2	0	371	958	678	166	425	0	995	25000	0.45	8	165	2191
22-1	63	300	963	706	165	570	0	1001	0	0.45	6	114	2177
22-2	63	300	963	709	165	285	547	0	0	0.45	6	102	2220
23-1	63	300	963	706	164	428	0	0	12500	0.45	7	178	2163
23-2	63	300	963	709	164	428	0	0	12500	0.45	8	102	2213
24-1	63	300	963	788	163	143	0	1001	25000	0.45	8	140	2241
24-2	63	300	963	709	164	285	0	0	25000	0.45	7	165	2213
25-1	132	236	992	730	167	294	588	0	0	0.45	7	108	2241
25-2	132	236	992	731	166	353	206	0	0	0.45	7	102	2206
26-1	132	236	992	730	166	441	0	0	12500	0.45	8	127	2227
26-2	132	236	997	726	166	353	0	0	12500	0.45	6	140	2241
27-1	132	236	992	730	166	147	0	0	25000	0.45	7	178	2262
27-2	132	236	997	726	166	176	0	0	25000	0.45	5	191	2305

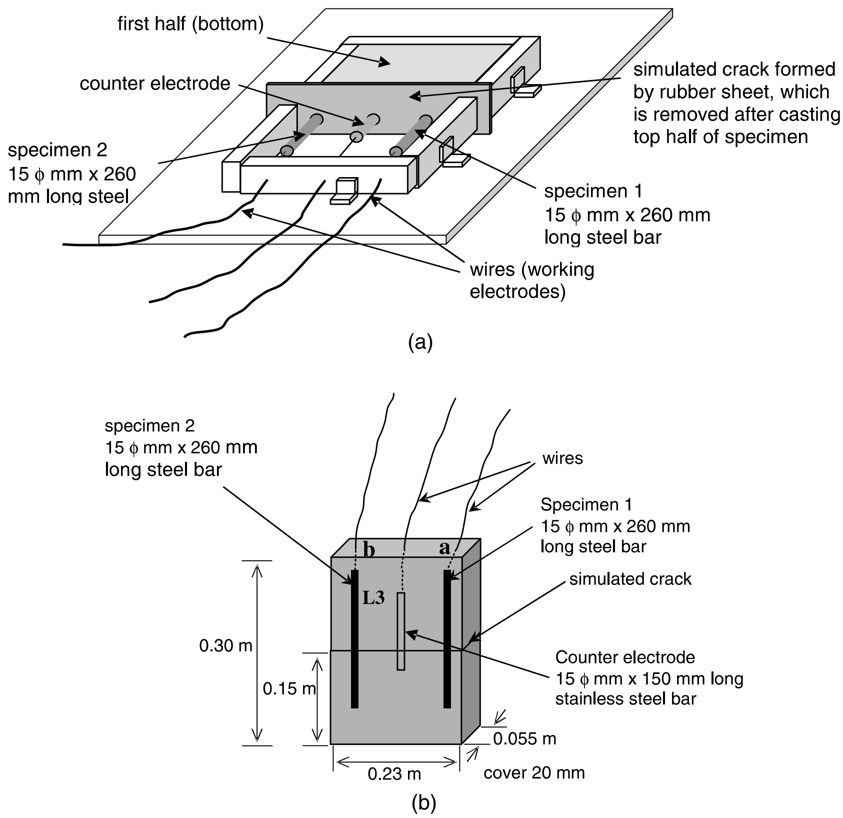

Fig. 1. Schematic diagram of concrete specimen.

environment and the reduction in tensile strength of the steel bars used in this experiment will be evaluated and reported. The specimen production process was therefore tailored for this larger objective.

To form a simulated crack, each corrosion test specimen was prepared in two halves. The first half of the specimen was prepared with a target slump of 100 mm and an air content of 7%, and on the following day a similar mixture of concrete was prepared for the second half of the corrosion test specimen. The mixture on the second day was adjusted slightly to bring the air content and slump as close as possible to the target values. The first half of the specimen was cast and demolded on the next day. Then, a 150×300 mm rubber sheet which was either 0.25 or 0.50 mm in thickness was placed to perform the crack [33]. To obtain a crack width of zero thickness the second day concrete was cast directly against the previous day casting which simulated a typical construction joint.

Twenty-seven concrete mixtures were prepared in total (Table 4) and three slabs were cast for each mixture proportion, the nominal dimensions of the concrete slabs were $55 \times 230 \times 300$ mm. The thickness and width of the specimens were adjusted to provide a cover of 20 ± 2 mm to accelerate the corrosion process. Fig. 1 shows a schematic of the concrete specimens. An air entrainment agent was added to the mixtures to compensate for the detrimental effects on the concrete due to the severe exposure conditions at the natural marine exposure site where two of the companion specimens have been exposed since the fall of 1999.

9. Experimental setup

To evaluate the effects of artificial seawater on corrosion of reinforcing bars embedded in concrete specimens, the marine environment simulation setup (MESS) Chambers at the University of New Brunswick was utilized to test one of the three companion specimens made from each mixture.

The MESS for accelerated testing consists of two chambers where it is possible to simulate wetting and drying cycles in concrete specimens in marine exposure conditions. Two complete cycles are performed within a 24-h period as compared with two tidal cycle in a natural marine environment. Also, the effect of temperature ranging from 26 ± 2 °C in the wet cycle to 55 ± 2 °C in the dry cycle is considered.

10. Experimental procedure

The corrosion activity of the reinforcing steel bars was monitored by using the linear polarization resistance

Table 5
Visual inspection of specimens

Fly ash (%)	CNI (L/m^3)	Crack width (mm)	#	0.29 w/c ratio, Time (months)						#	0.37 w/c ratio, Time (months)						#	0.45 w/c ratio, Time (months)					
				2	4	6	8	10	12		2	4	6	8	10	12		2	4	6	8	10	12
0	0	0	L1	–	–	–	–	–	–	L28	–	–	–	–	–	–	L55	–	–	–	b	a,b,cc	a,b,cc
		0.25	L2	–	–	–	a,b	a,b	a,b	L29	–	–	–	–	–,a,b,rt	–,a,b,rt	L56	–	–	–	a,b	a,b,cc	a,b,cc
		0.50	L3	–	–	–	a	a,b	a,b	L30	–	–	–	–	–,a,b,rt	–,a,b,rt	L57	–	–	–	a	a,b,cc	a,b,cc
	12.5	0	L4	–	–	–	–	b	b	L31	–	–	–	–	–	–	L58	–	–	–	a	a,b,*	a,b,cc*
		0.25	L5	–	–	–	–	b	b	L32	–	–	–	–	a	a,b	L59	–	–	–	a,b	a,b,cc	a,b,cc
		0.50	L6	–	–	–	a,b	a,b	a,b,rt	L33	–	–	–	a,b	a,b	a,b,rt	L60	–	–	–	a	a,b,cc	a,b,cc
	25	0	L7	–	–	–	–	–	–	L34	–	–	–	–	–	–	L61	–	–	–	a	a,b,cc,*	a,b,cc,*
		0.25	L8	–	–	–	b	b	b	L35	–	–	–	a	a,b	a,b	L62	–	–	–	a,b	a,b,cc	a,b,cc
		0.50	L9	–	–	–	b	b	b	L36	–	–	–	b	a,b	a,b,cc	L63	–	–	–	a,*	a,b,cc,*	a,b,cc,*
20	0	0	L10	–	–	–	–	–	–	L37	–	–	–	b	a,b	a,b	L64	–	–	–	a	a	a,b
		0.25	L11	–	–	–	–	b	b	L38	–	–	–	b	b	b	L65	–	–	–	a,b	a,b,cc	a,b,cc
		0.50	L12	–	–	–	–	–,*	–,*	L39	–	–	–	b	b	a,b,cc,rt	L66	–	–	–	a,b	a,b,cc	a,b,cc
	12.5	0	L13	–	–	–	–	–	–	L40	–	–	–	–	–	–	L67	–	–	–	–	a,b	a,b
		0.25	L14	–	–	–	–	–	–	L41	–	–	–	–	–	–	L68	–	–	–	b	a,b,cc	a,b,cc
		0.50	L15	–	–	–	–	–	–,rt	L42	–	–	–	–	b	b	L69	–	–	–	–	a,b	a,b
	25	0	L16	–	–	–	–	–	–	L43	–	–	–	–	–	–	L70	–	–	–	–	a	a,b
		0.25	L17	–	–	–	–	–	–	L44	–	–	–	–	–	a	L71	–	–	–	–	a,b,cc	a,b,cc
		0.50	L18	–	–	–	–	–	a,rt	L45	–	–	–	–	–	b	L72	–	–	–	–	a,b	a,b,rt
40	0	0	L19	–	–	–	–	–	–	L46	–	–	–	–	–	–	L73	–	–	–	–,*	–,*	b,*
		0.25	L20	–	–	–	a,b	a,b	a,b	L47	–	–	–	b	b	b	L74	–	–	–a,*	a,b,*	a,b,cc,rt*	
		0.50	L21	–	–	–	a,b	a,b	a,b,cc	L48	–	–	–	–	–	a,b	L75	–	–	–	a,b,*	a,b,*	a,b,*
	12.5	0	L22	–	–	–	–	–	–	L49	–	–	–	–	–	–	L76	–	–	–	–,*	–,*	a,*
		0.25	L23	–	–	–	–	–	–	L50	–	–	–	b	b	b	L77	–	–	–	a	a,cc	a,b,cc
		0.50	L24	–	–	–	–	a	a,cc	L51	–	–	–	a,b	a,b,cc	a,b,cc	L78	–	–	–	b,*	a,b,*	a,b,*
	25	0	L25	–	–	–	–	–	–	L52	–	–	–	–	b	b	L79	–	–	–	–,*	–,*	–,*
		0.25	L26	–	–	–	–	–	a	L53	–	–	–	–	b	b	L80	–	–	–	–,*	–,*	a,*
		0.50	L27	–	–	–	–	–	–	L54	–	–	b	a,b	a,b,cc	a,b,cc	L81	–	–	–	–,*	–,*	a,*

– = good condition, a = crack parallel to the reinforcement at bar a, * = concrete deteriorization, rt = rust from artificial cracks, cc = rust from cracks due to corrosion.

method. The equipment used for this purpose was CMS 105 (by GAMRY Instruments Inc.) with a concrete resistance compensation capability. A saturated calomel electrode (SCE) was used as a reference electrode. The proportionality constant B was assumed to be 26 mV in the calculation of the corrosion rate of the uncoated reinforcing steel as recommended by Alonso et al. [37]. The surface of the concrete slabs was also visually inspected on a regular basis and the existence of stains, additional cracks or concrete deterioration, if any, was noted throughout the testing program. The results are presented in Table 5.

11. Results and discussion

11.1. Cracking

Precracks as described in this section are those cracks preformed with a rubber membrane to simulate tensile cracks in a structural member, and cracking consists of cracks formed usually parallel to the reinforcing bar as a consequence of the corrosion process.

The percentage of cracked specimens due to corrosion was 25%, 35% and 60% corresponding to 0.29, 0.37 and 0.45 w/c ratio after eight months of exposure to the simulated aggressive environment (Table 5). After one year of exposure, these percentages had increased to 48%, 70% and 96% for the corresponding w/c ratios, indicating the clear influence that a low w/c ratio concrete has in preventing corrosion induced cracking.

For the 0.29 w/c ratio specimens, no cracking was observed for all the uncracked specimens. Only the precracked specimens containing the combination of 20% fly ash and 12.5 L/m^3 of CNI had no cracking.

With regard to the 0.37 w/c ratio, only the uncracked specimens and those containing the combination of 40% fly ash and 25 L/m^3 of CNI experienced no cracking. For 0.45 w/c ratio, cracking was observed in most of the specimens, regardless of the presence of a preformed crack, CNI or fly ash, except by those containing the combination of 40% fly ash and 25 L/m^3 of CNI. However, for this case significant rust was observed coming from the preformed crack.

It was also found that the use of 12.5 L/m^3 of CNI and 20% of fly ash alone and in combination helps to minimize cracking, which is specially evident in 0.29 w/c ratio. Another finding from this study was that the increment of fly ash from 20 to 40% and CNI from 12.5 L/

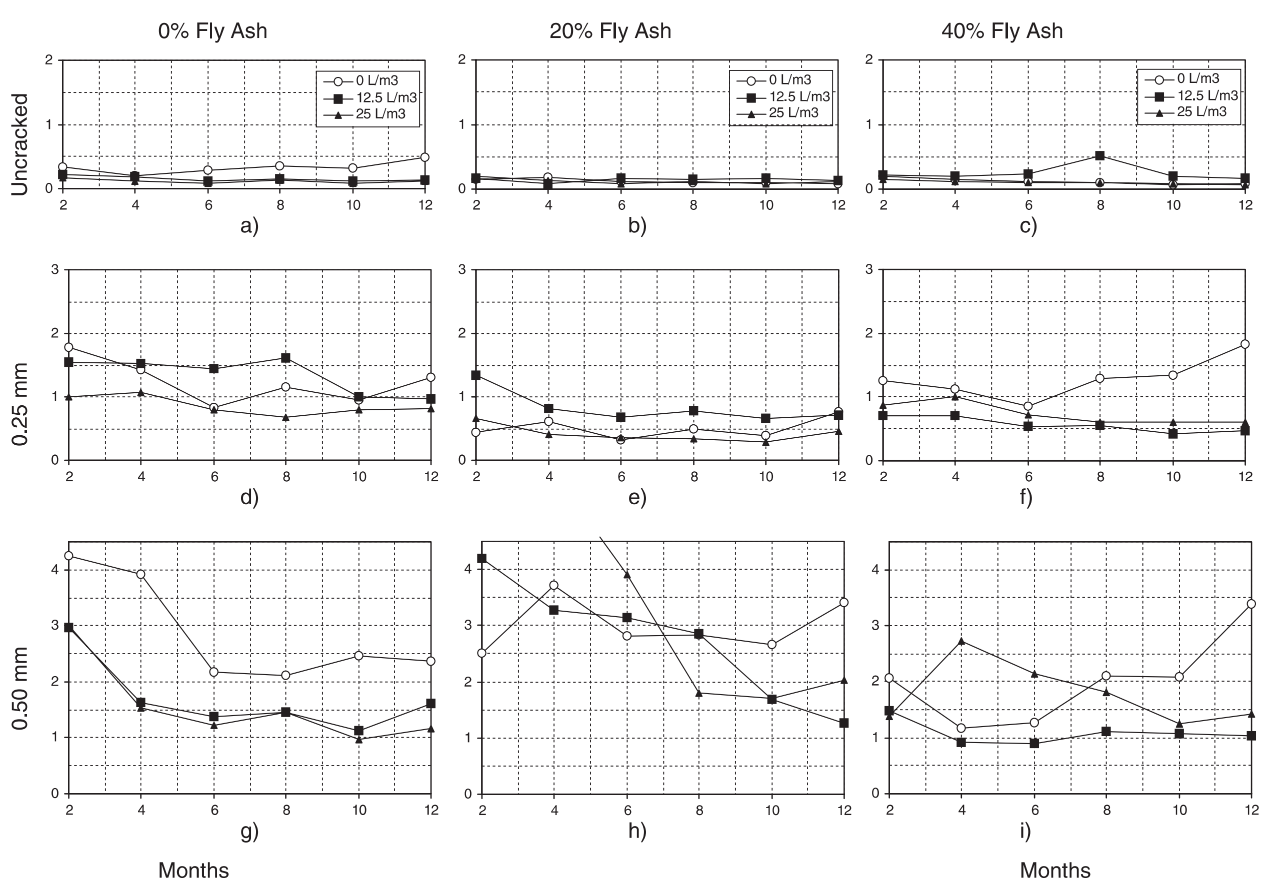

Fig. 2. Corrosion current densities for 0.29 w/c specimens (μA/cm^2).

m^3 to 25 L/m^3 does not improve the resistance to cracking.

12. Corrosion

12.1. Uncracked specimens

The linear polarization readings for most of the uncracked specimens (i.e. specimens with a simulated construction joint) were less than 0.5 $\mu A/cm^2$, which suggests a passive condition of the steel over the testing period according to Broomfiedl [2]. In general, the effect of CNI is not identifiable in uncracked specimens due to the small corrosion current density registered (graphs a–c in Figs. 2 and 3). Only for the 0.45 w/c ratio containing 20% fly ash a slight positive effect of CNI was observed (Fig. 4b). However, fly ash was effective in decreasing corrosion for uncracked 0.45 w/c ratio specimens as suggested by Fig. 4a–c.

12.2. 0.25 mm crack specimens

The 0.25 mm crack specimens presented moderated to high corrosion condition for most of the cases over the testing period (values ranging between 0.5 and 1.8 $\mu A/cm^2$, as shown in graphs d–f in Figs. 2 and 3). For the 0.45 w/c ratio values as high as 3 $\mu A/cm^2$ were recorded (Fig. 4d–f). A slight decrease in corrosion for 0.37 w/c ratio specimens was noted under this crack condition as compared to specimens made with higher and lower w/c ratios. Also, a clear positive effect of CNI in decreasing the corrosion for the specimens containing fly ash was observed, this is specially true for a 0.45 w/c ratio (Fig. 4e and f). Finally, a slight beneficial effect of fly ash in decreasing corrosion for the 0.25 mm crack specimens was observed.

12.3. 0.50 mm crack specimens

For the 0.50 mm crack width most of the specimens presented high corrosion condition (as high as 7 $\mu A/cm^2$). For these specimens, no identifiable influence of w/c ratio on the corrosion results was detected. A significant beneficial effect of CNI for 0.5 mm crack specimens was detected with the 0.45 w/c ratio (graphs 4g–i). Moreover, the corrosion current density values registered for the majority of these specimens indicate high corrosion activity regardless of the mixture used. Finally, the influence of fly ash on the corrosion results for

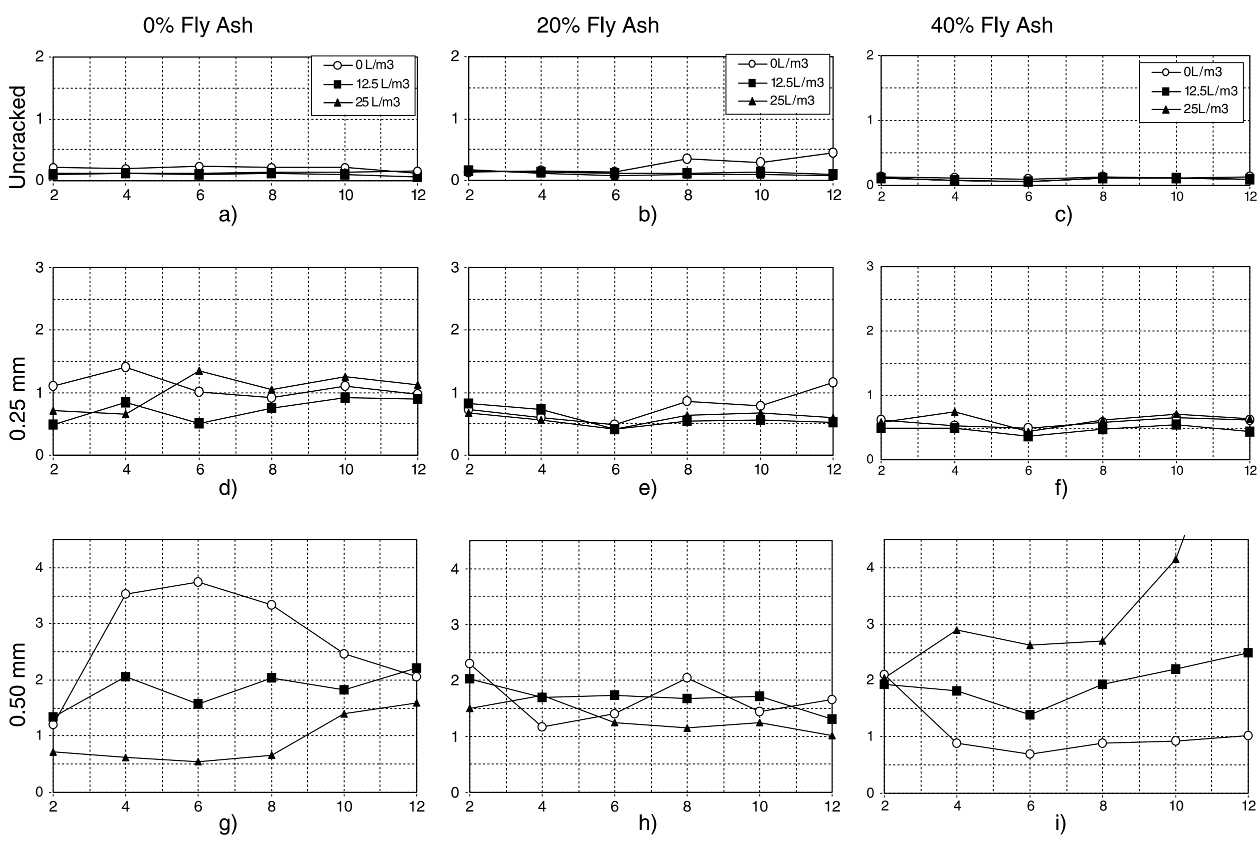

Fig. 3. Corrosion current densities for 0.37 w/c specimens ($\mu A/cm^2$).

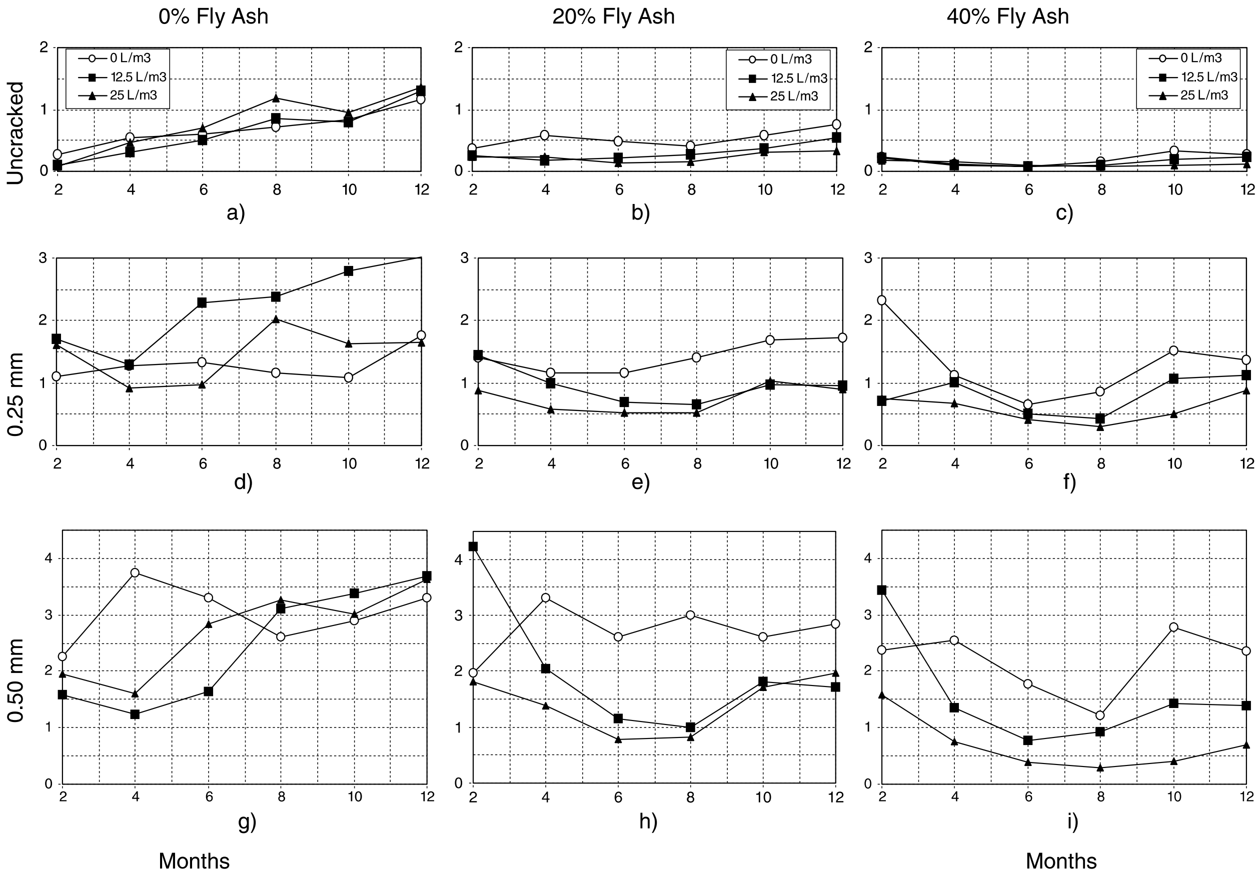

Fig. 4. Corrosion current densities for 0.45 w/c specimens (μA/cm²).

this condition was not easily identifiable for w/c 0.29 and 0.37 specimens (graphs g–i in Figs. 2 and 3).

13. Conclusions

Based on the results of the experimental program the following conclusions are drawn:

The w/c ratio plays an important role in the development of cracking due to corrosion. The lower the w/c ratio, the less cracking to be expected, and this effect is more evident when fly ash and CNI are included in the low w/c ratio mixture. This suggests that the combination of low permeability concrete and corrosion protection of the steel using CNI together is effective in reducing cracking in concrete, by decreasing cracking–corrosion interaction phenomenon.

With regard to Linear Polarization Resistance results, it is concluded that cracking of the concrete strongly affects the rate of corrosion, reaching values as high as ten time its uncracked condition.

In general, for the concrete characteristics and exposure conditions evaluated in this work, it was found that CNI alone does not always provide corrosion protection of the steel reinforcement in concrete. Even for uncracked concrete without fly ash in a 0.45 w/c ratio concrete, CNI failed to prevent corrosion. However, 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.

14. Continuing research

More research is needed on various corrosion prevention methods for long-term exposure conditions and these studies, now in the planning stage and involving structural members, will be carried out at the marine exposure site. The results obtained from this research will be compared with the ongoing long-term experiments in the marine exposure at Treat Island, Maine and the results will be reported later.

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