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Compressive strength of HPC containing CNI and fly ash after long-term exposure to a marine environment

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ABSTRACT

This study addressed the effect of calcium nitrite based corrosion inhibitor (CNI) and fly ash (FA) on the long-term compressive strength of high performance concrete (HPC). A 3^3 full factorial design was developed to evaluate the influence of CNI at addition rates of 0, 12.5 and 25 L/m^3 on the compressive strength of HPC manufactured with 8% silica fume blended cement in combination with 0%, 20% and 40% FA replacements and mixed at 0.29, 0.37 and 0.45 water to cementing materials ratios (w/cm). Standard 100 × 200 mm cylinders were prepared and tested for compressive strength at 28 days and 1 year. The 9-year old concrete specimens were obtained from small-scale reinforced concrete slabs that were exposed to a marine environment. Results indicate that the interaction of CNI and FA does not adversely affect the short and long term compressive strength of concrete. In fact, an enhancement on the compressive strength was observed in concretes containing such combination even after long-term exposure to a marine environment.

1. Introduction

The strength of concrete is one of its most important engineering properties because it not only reflects its mechanical quality, but in general it also provides an indication of its durability [1]. Calcium nitrite (CNI) has been used extensively in North America since 1978 to provide corrosion protection to the steel reinforcement [2,3]. Due to its chemical properties CNI enhances the compressive strength of concrete at an early age, and accelerates its setting time within the range recommended by standards [4,5]. However, it has been suggested that concrete in contact with high concentrations of calcium nitrite at relatively high w/cm could experience mortar deterioration [6]. Also, some studies have shown that the use of CNI in the presence of silica fume and fly ash can have a negative effect on the long-term strength of concrete [7,8]. Conversely, other studies have concluded that the CNI addition, alone or in combination with supplementary cementing materials, has a positive effect on the compressive strength of concrete at early and late ages [9–13].

To investigate this further, in this study the compressive strength of concrete prepared with CNI and fly ash after long-term exposure to a marine environment is investigated. This work is part of a larger program that evaluates the influence of CNI and fly ash on the corrosion protection of uncracked and cracked reinforced concrete [14]. A series of 27 mixtures with and without CNI in combination with fly ash and 8.2% silica fume, at 3 w/cm, were prepared and tested in compression at 28 days, 1 year, and after 9 years after exposure to a marine environment. Comparative results of the three ages studied are presented. The effects of the three main components of the mixtures, (i.e. w/cm, fly ash, and CNI) and their interactions, on the long-term compressive strength are also analyzed. To provide a better understanding of the influence of the main components of the mixtures on the compressive strength of concrete a brief discussion follows.

1.1. Water to cementing materials ratio

The properties of concrete are largely governed by the cementitious matrix and the strength of concrete is basically dictated by the capillary porosity, which is a function of the w/cm and degree of hydration of the cement particles. A high w/cm concrete contains a larger capillary pore space than a low w/cm concrete. This effect has an important influence on the strength of the hardened paste, which is the dominant factor in the strength of concrete. In other words, the strength of concrete mainly resides in the strength of the paste [15].

In concrete containing CNI, the w/cm is a factor that influences not only the corrosion inhibition properties but also the compressive strength. It has been reported that at w/cm below 0.50 the

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effectiveness of CNI in concrete gives especially good performance [16]. It has been realized for a long time, notably by Brown [17] that CNI enhances the compressive strength of concrete at an early age; however, the long-term compressive strength of concrete containing CNI has been scarcely documented. Moreover, as summarized in Table 1, most of the studies on the related research have been carried out on concretes prepared with w/cm of 0.40 or higher, and limited research on the use of CNI in lower w/cm concretes (i.e. high performance concrete) has been undertaken [12]; therefore, further research is of special interest.

Table 1
Literature review on CNI-concrete related research.

Refs.	Age of test (days)	w/cm	Cement	CNI content	SCM amount	Findings
Montes et al. [12]	28	0.29 0.37 0.45	PC + 8.2% SF	0 L/m^3 12.5 L/m^3 25 L/m^3	0% FA 20% FA 40% FA	• Increase of approximately 15% in f′c for all w/cm with 12.5 L/m^3 of CNI • Increase in 8, 21 and 32% compressive strength for 0.29, 0.37 and 0.45 w/cm, respectively, when 25 L/m^3 CNI was used
Ann et al. [13]	7, 28, 60 and 900	0.5	OPC	0, 3, 6 L/m^3 and 12 L/m^3		• At 7, 28, and 60-day compressive strength was 10% higher than control specimens. However, at 900 days all concretes with CNI showed a decrease in strength to levels of 28 days
Brown et al. [17]	3,7, 28, and 365	0.45	Type I or Type I/II	14.85 L/m^3		• An increase of 26, 38, 21 and 16% in compressive strength at 3, 7, 28, and 365 days respectively, when CNI was added
Reou and Ann [22]	7, 28, 56, 91, 180 and 365	0.45	OPC, PFA and GGBS	0%, 2%, 3%, and 4% (weight of cement)	30% FA 65% GGBS	• The strength increased with time regardless the CNI addition and binders • OPC with CNI was the highest compressive strength, followed by PFA and GGBS
De Rincon et al. [23]	28	0.45 0.5 0.6	PC I	2%, 3%, 4% (weight of cement)		• Compressive strength was higher with 4% of CNI addition for all w/cm
Al-Amoudi et al. [24]	28	0.45	C 150 Type V	0%, 2%, 4% (weight of cement)		• Increase of approximately 8–9% in compressive strength, with respect to control, when 2 and 4% of CNI was added
De Schutter and Luo [25]	3, 7, and 28	0.45	PC CEM I Slag CEM III/A	0 L/m^3 and 5 L/m^3		• The strength at 7 and 28 days was higher than control when 5 L/m^3 CNI was used • At 28 days the strength was unchanged for CEM I and a reduction of 6% in slag cement was found
Kondratova et al. [26]	7,28 and 91	0.4	PC Type 10	0 L/m^3 and 25 L/m^3		• No noticeable effect on the compressive strength with the CNI addition was found
Civjan et al. [27]	28	0.4 0.47	PC Type I/II cement	14.8 L/m^3	6% SF, 15% FA 25%BFS	• An increase in strength of about 15% was noted for concretes containing CNI in combination with SF, FA and/or BFS
Berke et al. [28]	1 and 28	0.4 0.5	PC Type V	5 L/m^3 and 20 L/m^3		• One-day strength of 0.4 w/cm concrete with 5 and 20 L/m^3 CNI increased by 13 and 19.7%. For 0.50 w/cm concrete containing 20 L/m^3 of CNI the increment was 29% • 28-day strength of 0.4 w/cm concrete with 20 and 5 L/m^3 CNI increased by 2 and 9%. For 0.50 w/cm concretes the increment was 2 and 8.6% in concretes containing 5 and 20 L/m^3 of CNI, respectively
Berke et al. [29]	28	0.49	PC Type I	10 L/m^3 and 20 L/m^3		• An increase in strength of about 12% and 34% with respect to the control was noted in concretes contained 10 and 20 L/m^3, of CNI, respectively
Sideris and Savva [30]	7 and 28	0.42	CEM II32.5 blended cement	20 L/m^3	10–30% NP 10–15% SF 10–30–40% FA	• The addition of 20 L/m^3 of calcium nitrite slighly increased the compressive stregth of all admixtures at the age of 7 and 28 days

SMC, supplementary cementing materials; OPC, ordinary portland cement; FA, fly ash; SF, silica fume; GGBS/BFS, ground granulated blast furnace slag; CNI, calcium nitrite based corrosion inhibitor.

1.2. Fly ash replacement

Fly ash is a finely-divided amorphous alumino-silicate material with particle size ranges between 1 and 150 μm. When mixed with portland cement and water, fly ash contributes to the properties of the micro-structure of concrete through hydraulic or pozzolanic activity, or both [18]. During the pozzolanic reaction, calcium hydroxide $Ca(OH)_2$ released by the hydration of portland cement, is transformed into additional C–S–H gel and calcium–aluminate hydrates [19].

Fly ash when rationally used in combination with portland cement contributes to the fresh and hardened concrete by improving properties such as workability, reduction of bleeding, heat of hydration, permeability among others. On the other hand, reduction of compressive strength of concrete at early ages is experienced; however, long-term strength development is improved and at some age the compressive strength of the fly ash concrete will equal that of the portland cement concrete so long as adequate curing is provided [18]. Also, more long-term benefits result from using fly ash in concrete, for example it makes it more resistant to the penetration of aggressive agents by enhancing the micropore refinement of the concrete matrix [20,21].

1.3. CNI corrosion inhibitor amount

Although several studies have been published on the use of CNI in concrete, most of them focused on the corrosion inhibition effects rather than the development of the mechanical properties such as compressive strength. Furthermore, as can be seen in Table 1, the effects of the combination of CNI with fly ash and silica fume on the long-term strength of concrete have been scarcely reported. The existing information in this respect is controversial because some studies conclude that the use of CNI may be detrimental to the strength development in the long term [13]. However, others claim that the addition of CNI to concrete has been found to be non-detrimental to the mechanical properties of concrete and is reported to be compatible with silica fume and fly ash [10]. Also, a reduction of micropore refinement caused by the secondary hydration reaction of fly ash and the reduction in compressive strength by the inclusion of CNI have been reported by others as well [8]. In the light of the above discussion, is clear that the study of the long-term properties of fly ash concrete in combination with such chemical admixtures as corrosion inhibitors is limited to date and even in the limited research available the conclusions appear at time to be in conflict; therefore, further research is appropriate.

2. Materials and methods

2.1. Design of the experiment

A full 3^3 factorial design was selected to examine the effect of the combination of 0%, 20% and 40% fly ash replacements and CNI at 0, 12.5 and 25 L/m^3 in concretes prepared at 0.25, 0.37 and 0.45 w/cm on the compressive strength of concrete. The response variables were compressive strength at 28 days, 1 year and after 9 years of age. Details of the experimental design are show in Table 2.

Table 3
Chemical and physical analysis of SF portland cement and fly ash.

Chemical composition	Test result	
	8.2% SF PC	Fly ash
Silica (SiO_2)	26.70%	35.00%
Alumina (Al_2O_3)	4.00%	15.20%
Iron oxide (Fe_2O_3)	2.90%	31.40%
Calcium oxide, total (TCaO)	59.60%	1.71%
Magnesium oxide (MgO)	0.90%	1.62%
Sulphur trioxide	2.70%	2.01%
Loss of ignition	1.70%	2.03%
Calcium oxide, free (FCaO)	1.50%	
Equivalent alkali (as Na_2O)	0.46%	1.70%
Carbon, %		0.45%
Physical analysis		
Fineness 45 mm sieve	94.3% passing	13.2% retained
Blaine (Spec. surf)	555 m^2/kg	
Vicat setting time	125 min	
Autoclave expansion or contraction	0.0%	0.03%
Moisture content, %		0.15%
Specific gravity		2.50%
Water requirement % of control		95%
Potential compounds		
C_3A	5.70%	

2.2. Concrete materials and properties

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

2.2.1. Cementing materials

2.2.1.1. Portland cement. CSA Type GUB-8.5 SF Portland cement (ASTM Type I) [31] with 8.2% silica fume cement replacement was used for all the mixtures.

2.2.1.2. Fly ash. The fly ash used was Type F according to the ASTM classification [31]. The physical and chemical characteristics of portland cement and fly ash are given in Table 3.

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

2.2.2. Chemical admixtures

The chemical admixtures used were air entraining admixture (ASTM C 260), retarding admixture (ASTM C 494 Type D) and High Range Water Reducer (ASTM C 494, Type F) [31].

2.2.2.1. Calcium nitrite based corrosion inhibitor. The commercial calcium nitrite based CNI used in this study contains a minimum of 30% calcium nitrite and includes a set retarder.

2.3. Mixture proportions and specimen preparation

Twenty-seven concrete mixtures were prepared in total. The detailed mixture proportions and properties of the concrete in its fresh and hardened state are given in Table 4. Eight cylindrical specimens ($100\phi \times 200$ mm) for each mixture were prepared

Table 2
Selection of factors investigated in the experiment.

Factors	No. of levels	Description	Response
Water/cement ratio	3	0.29, 0.37 and 0.45	Compressive strength (28 days, 1 year and 9 years)
Fly ash content	3	0%, 20% and 40%	
Corrosion inhibitor percentage	3	0, 12.5 and 25 L/m^3	

Table 4
Nominal mixture proportions.

Mixture number	Fly ash (kg/m^3)	Cement + SF (kg/m^3)	CA (kg/m^3)	FA (kg/m^3)	Water (kg/m^3)	CNI (L)	w/cm	Air (%)	Slump (mm)
1	0	544	1029	664	154	0	0.29	4.0	165
2				664	155	12.5		5.5	160
3				664	155	25		4.5	200
4	87	422	992	646	148	0		6.0	180
5				646	148	12.5		7.0	190
6				646	149	25		7.0	170
7	177	317	987	650	145	0		7.5	115
8				650	145	12.5		7.5	130
9				650	145	25		7.0	160
10	0	441	997	702	164	0	0.37	7.0	150
11				702	164	12.5		6.0	170
12				702	164	25		6.0	150
13	73	351	985	694	158	0		8.0	110
14				694	158	12.5		7.0	130
15				694	157	25		7.5	135
16	150	268	993	699	155	0		8.0	120
17				699	156	12.5		7.5	120
18				699	155	25		7.5	150
19	0	371	957	703	169	0	0.45	8.0	120
20				705	167	12.5		7.0	130
21				705	167	25		7.5	150
22	63	300	963	706	165	0		6.0	110
23				706	164	12.5		7.5	140
24				788	163	25		7.5	150
25	132	236	992	730	167	0		7.0	105
26				730	166	12.5		7.0	135
27				730	166	25		6.0	185

Note: CA and FA mean coarse aggregate and fine aggregate respectively.

according to ASTM C192/C 192M-98 [28] for compressive strength testing. Six specimens were tested at 28 days according to ASTM C39/C39M standards [31] and the results were reported accordingly [12]. The remaining two cylinders were kept in the curing room and tested after 1 year for 0.29 and 0.45 w/cm mixtures. For 0.37 w/cm mixtures, only one specimen was tested in compression and the second was retained for air void spacing.

The 9 year old concrete specimens were obtained from 27 small-scale reinforced concrete slabs ($55 \times 230 \times 300$ mm) that were moist cured for 7 days in laboratory conditions and then exposed to a marine environment at the Corps of Engineers facilities, located in Maine, USA. After 7 years the concrete slabs were retrieved and returned to the University of New Brunswick laboratory where they were stored for 2 years while being evaluated for damage caused by corrosion; then, 162 cubes, six per slab with 50×50 mm per side were sawed and ground to achieve flat parallel sides for subsequent compressive strength testing.

All prismatic specimens were tested in a hydraulic compression tester INSTRON® 5500 with a closed-loop servo control and a capacity of 5000 kN. In the analysis of results, the average of six concrete specimens was used. Additionally, carbonation front evaluation by spraying 1.0% w/v phenolphthalein ethanol (90) solution was conducted on all the concretes. Results of the carbonation test showed a negligible effect of this deterioration process in all the concretes. Therefore, specimens should not experience reductions in the compressive strength caused by carbonation or frost action since, as reported in Table 4, the average air void content in the mixtures was about 6.8%.

3. Results

3.1. Twenty eight-day compressive strength results

Results of the 28-day compressive strength obtained from standard cylindrical concrete specimens are summarized in Table 5.

The 28-day compressive strength results are plotted against FA replacements in Fig. 1. Results show that when fly ash was used to replace portland cement with 8.0% silica fume, the 28-day

Table 5
Compressive strength results in MPa at 28 days.

w/cm	Fly ash content								
	0% Fly ash			20% Fly ash			40% Fly ash		
	Calcium nitrite content (L/m^3)								
	0	12.5	25	0	12.5	25	0	12.5	25
0.29	72.0[a] (5.8) 1	82.2 (4.5) 2	77.8 (7.4) 3	61.8 (3.1) 4	67.1 (4.8) 5	66.5 (6.9) 6	41.7 (5.7) 7	53.6 (2.9) 8	51.2 (2.3) 9
0.37	53.5 (6.0) 10	62.1 (1.7) 11	65.0 (3.3) 12	42.7 (4.8) 13	46.4 (4.7) 14	50.3 (1.9) 15	30.9 (4.6) 16	37.9 (2.1) 17	39.6 (6.0) 18
0.45	33.9 (1.5) 19	38.8 (2.8) 20	45.0 (1.7) 21	33.4 (2.7) 22	31.3 (4.5) 23	41.6 (3.9) 24	26.2 (5.8) 25	26.9 (0.6) 26	31.9 (1.8) 27

Notes: Number at the top are results on average of six specimens (cylinders 100×200 mm), numbers inside parentheses are standard deviation, and numbers beside parenthesis are the mixture reference number.
[a] 0.28 w/cm.

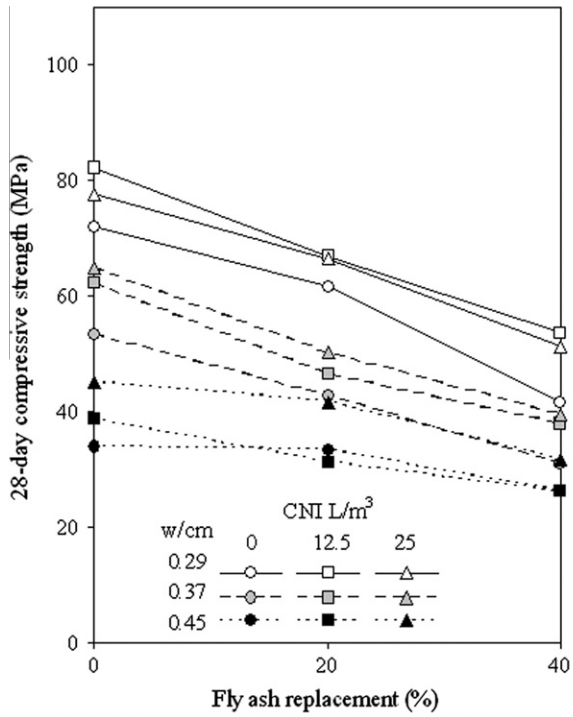

Fig. 1. Effect of the main constituents of concrete on the 28-day compressive strength.

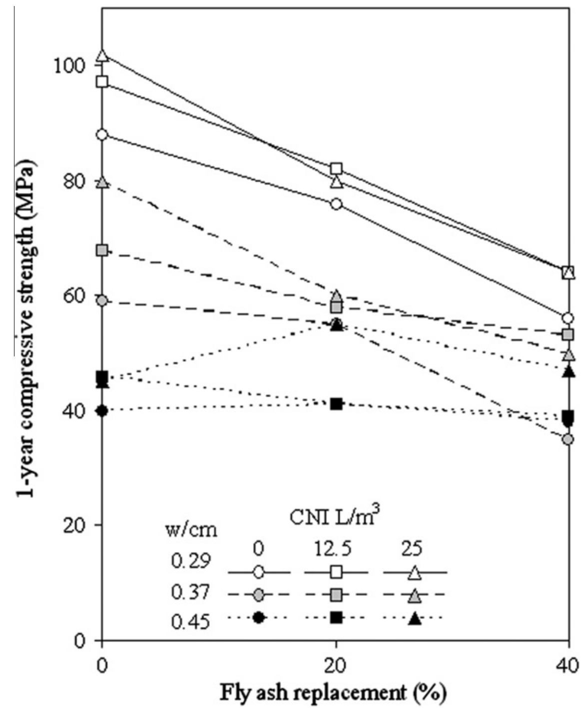

Fig. 2. Effect of the main constituents of concrete on the 1-year compressive strength.

compressive strength of the concrete decreased considerably. Also, from Fig. 1 it is possible to observe the great influence that the w/cm has on the compressive strength of concrete, the smaller the w/cm, the higher the compressive strength, even in concretes with a higher FA replacement. It is also interesting to note that the addition of 25 L/m^3 in 0.45 w/cm concretes has a significant positive effect on the compressive strength, conversely in low w/cm concretes of 0.37 and 0.29 such effect is less pronounced. Furthermore, in 0.29 w/cm concretes a slightly decrease in the compressive strength was observed when compared with concretes containing only 12.5 L/m^3 of CNI.

3.2. One-year compressive strength results

The 1-year compressive strength results are summarized in Table 5. As expected, all the 1-year compressive strength values were higher than those obtained from 28-day testing (see Table 6).

Fig. 2 shows the effect of the w/cm, CNI amounts, and fly ash replacements on the 1-year compressive strength of concrete. Results show that, all the 1-year compressive strength values were higher than the 28-day compressive strength for the 3 w/cm studied. The highest compressive strength values were observed for concrete mixtures containing higher amounts of CNI. Similar results were also observed by Reou and Ann [22] in concrete specimens manufactured with blended cements in combination with 0.0%, 1.0%, 2.0%, and 3.0% CNI by weight of binder. Conversely, Brown et al. [17] found that the 1-year compressive strength of concretes containing 14.85 L/m^3 CNI were slightly lower that concrete specimens tested at 28-day of age.

From Fig. 2, it is also possible to see that similarly to 28-day results, the 1-year compressive strength tended to decrease when the percentage of fly ash replacement increased. However, this effect was more pronounced in specimens prepared at 0.29 w/cm, and seems to be less significant when the w/cm increased. In fact, in 0.45 w/cm concretes prepared without CNI and those containing 12.5 L/m^2 CNI, neither reduction nor significative increase in the compressive strength was observed with the FA addition.

3.3. Nine-year compressive strength results

As stated earlier, six cubes per mixture of approximately 50 mm per side were tested for 9-year compressive strength. In order to elucidate the occurrence or not of detrimental reactions between

Table 6
One-year compressive strength in MPa.

w/cm	Fly ash content								
	0% Fly ash Calcium nitrite content (L/m^3)			20% Fly ash			40% Fly ash		
	0	12.5	25	0	12.5	25	0	12.5	25
0.29	87.9[a]	96.7	101.5	76.1	82.1	80.5	56.2	63.9	64.3
0.37	58.6	68.2	80.2	55.2	58.3	59.5	35.1	53.4	49.8
0.45	40.1	45.6	45.0	40.6	40.8	55.4	38.5	39.2	47.2

[a] 0.28 w/cm.

Table 7
Results of the 9-year compressive strength in MPa corrected for size and shape.

w/cm	Fly ash content								
	0% Fly ash			20% Fly ash			40% Fly ash		
	Calcium nitrite content (L/m^3)								
	0	12.5	25	0	12.5	25	0	12.5	25
0.29	84.0 (4.1)	87.1 (4.6)	84.6 (7.11)	76.3 (3.8)	71.9 (3.1)	75.4 (5.3)	64.3 (5.9)	70.8 (9.7)	68.9 (3.2)
0.37	61.8 (3.6)	69.8 (7.0)	71.2 (5.0)	56.5 (4.6)	58.2 (2.3)	56.3 (2.6)	49.1 (6.4)	52.3 (5.0)	60.3 (5.6)
0.45	32.8 (1.8)	40.3 (2.5)	43.8 (3.0)	44.4 (2.7)	41.6 (1.4)	51.2 (3.6)	40.1 (4.0)	47.5 (4.6)	55.7 (5.8)

Note: Results are based on average of six specimens (Cubes 50 × 50 × 50 mm) corrected to 100ϕ × 200 mm cylinder. Numbers in parentheses are standard deviation.

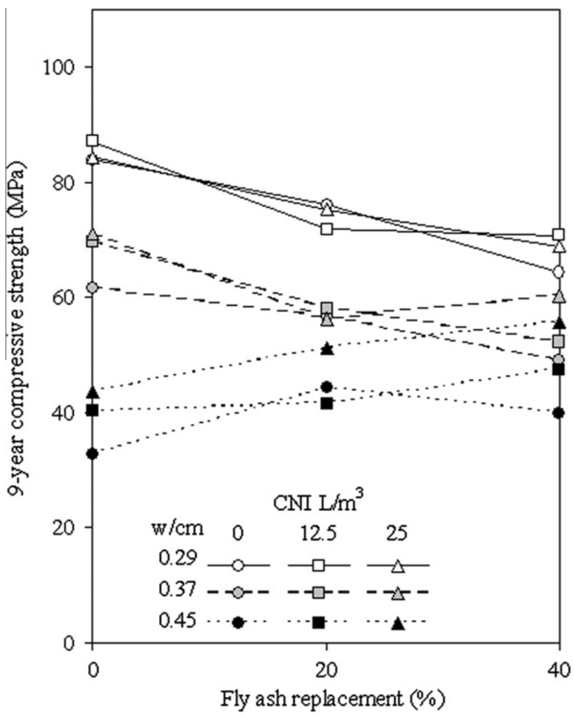

Fig. 3. Effect of the main constituents of concrete on the 9-year compressive strength.

the constituents of the mixtures as compared with the results obtained from cylinders tested at 28 days and 1 year, the 9-year compressive strength results obtained from cubes were corrected by size and shape using Eq. (1) as suggested by Del Viso et al. [32].

$$f'c = \sigma_{\text{cub}}\sqrt{\frac{L}{L+L_0}} \quad (1)$$

where σ_{cub}, is the compressive strength obtained during the test in MPa, L is the side of the cube in mm, and L_0 is an empirical constant dependent on the specimen shape. The 9-year compressive strength after the size and shape corrections is shown in Table 7.

Fig. 3 shows the effect of the w/cm, CNI amounts, and fly ash replacements on the 9-year compressive strength. Results showed that in concretes prepared at 0.29 and 0.37 w/cm, a reduction on the compressive strength was observed when 20% and 40% FA was added to the mixtures. However, this reduction is less pronounced than that obtained in concretes tested at 28 days and 1 year. Furthermore, it is interesting to note that in concretes prepared at 0.45 w/cm, a significant increase on the compressive strength was observed as the replacement of FA increased.

In concrete specimens containing CNI, either slightly or not significative increased on the 9-year compressive strength was observed in concretes prepared at 0.29 and 0.37 w/cm. In contrast, in concrete specimens containing 20% and 40% FA, the combination of 25 L/m^3 of CNI were significantly beneficial.

3.4. Effect of main components of the mixture at different ages

Table 8 shows the effects of the main components of the mixtures on the compressive strength of concrete at three different ages. The values were compared against the controls and decrements or increments in the compressive strength caused by the w/cm, fly ash replacement, and CNI addition are presented in percentages. The results demonstrate the importance of the w/cm on the compressive strength of concrete. A significative decrease in the strength from 13% to a maximum 61% was observed by increasing the amount of water in the mixture from 0.29 to 0.45 w/cm.

Columns 8–10 in Table 8 show the effect of 0%, 20% and 40% fly ash replacements on the compressive strength of concrete at different ages. In general a decrease in the compressive strength was observed for most of the mixtures as the fly ash replacement increase. In specimens tested at 28 days and 1 year, a reduction of maximum 26% and 42% in strength was observed respectively when 20% and 40% fly ash were incorporated in the mixture.

As far specimens tested at 9 years are concern, reductions ranging from 21% to 26% were observed in concretes prepared at 0.29 and 0.37 w/cm. Conversely, in concretes prepared at 0.45 w/cm, there was actually an increase in the compressive strength of maximum 33% and 21%, with respect to the controls, was observed when 20% and 40% fly ash replacements were used, respectively. From this finding it is possible to corroborate the beneficial effect of the use of fly ash on the long-term compressive strength gain of concrete suggested by Hassan et al. [33] who concluded that the compressive strength of FA concrete gave the lowest compressive strength at early ages as compared with similar mixture prepared with ordinary portland cement. However, FA concrete showed similar strength to that of the OPC mix at 28 days and higher value at 1 year.

In general, a positive effect of the incorporation of the CNI on the compressive strength of most of the mixtures was observed. In concretes tested at 28 days and 1 year, when 12.5 L/m^3 of CNI was incorporated into the mixture an increase in compressive strength of approximately 15–17% was noted for all the w/cm. When 25 L/m^3 of CNI was used, in concretes tested at 28 days a maximum increase in compressive strength of 8%, 23%, and 32% for 0.29, 0.37 and 0.45 w/cm concrete respectively, was observed. In concretes tested at 1 year a maximum increase in compressive strength of 16%, 36%, and 13% for 0.29, 0.37 and 0.45 w/cm concrete was observed, respectively.

A more detailed analysis indicate that in concrete specimens tested at 9 years, when 12.5 L/m^3 of CNI was added to a concrete mixture an increase in compressive strength of 4%, 13%, 23% for 0.29, 0.37 and 0.45 w/cm concrete, respectively. And an increase

Table 8
Effects of main constituents on the compressive strength at different ages.

Mixture number	w/cm	Fly ash (%)	CNI (L/m^3)	w/cm			Fly ash			CNI		
				28 d	1 year	9 year	28 d	1 year	9 year	28 d	1 year	9 year
1	2	3	4	5	6	7	8	9	10	11	12	13
M1	0.29	0	0	–	–	–	–	–	–	–	–	–
M2			12.5	–	–	–	–	–	–	14	10	4
M3			25	–	–	–	–	–	–	8	16	1
M4		20	0	–	–	–	−14	−14	−10	–	–	–
M5			12.5	–	–	–	−18	−15	−17	8	8	−5
M6			25	–	–	–	−15	−22	−12	6	5	−1
M7		40	0	–	–	–	−42	−36	−24	–	–	–
M8			12.5	–	–	–	−34	−34	−18	29	14	11
M9			25	–	–	–	−35	−37	−19	21	14	8
M10	0.37	0	0	−26	−33	−26	–	–	–	–	–	–
M11			12.5	−24	−30	−20	–	–	–	17	15	13
M12			25	−17	−22	−16	–	–	–	23	36	15
M13		20	0	−31	−28	−25	−19	−7	−8	–	–	–
M14			12.5	−31	−29	−19	−26	−15	−17	7	5	2
M15			25	−24	−25	−25	−23	−25	−21	16	9	−2
M16		40	0	−26	−38	−23	−42	−41	−21	–	–	–
M17			12.5	−30	−17	−27	−39	−22	−26	23	51	6
M18			25	−22	−22	−13	−38	−38	−15	29	43	22
M19	0.45	0	0	−53	−55	−61	–	–	–	–	–	–
M20			12.5	−52	−53	−54	–	–	–	15	15	21
M21			25	−42	−56	−48	–	–	–	32	13	33
M22		20	0	−47	−46	−42	−3	3	33	–	–	–
M23			12.5	−54	−50	−42	−21	−11	5	−6	0	−5
M24			25	−36	−31	−32	−7	22	16	27	34	16
M25		40	0	−38	−32	−38	−24	−5	21	–	–	–
M26			12.5	−50	−39	−32	−31	−15	20	4	3	20
M27			25	−37	−27	−19	−29	4	27	23	24	40

Note: Values in columns 5–13 are percentages of decrement or increment in compressive strength versus the controls.

in strength of 1%, 15%, and 34% for 0.29, 037 and 0.45 w/cm concrete, respectively, was noted when 25 L/m^3 of CNI was added.

The results listed in Table 8 (column 13), also show a slightly reduction in the 9 years compressive strength ranging from 1% to 5% in concrete specimens prepared with 12.5 or 25 L/m^3 CNI in combination with 20% fly ash.

4. Discussion

The influence of w/cm on the short-term and long-term compressive strength of CNI concrete has been demonstrated by these experimental data. This is illustrated in Fig. 4 in which the variations in compressive strength values with the type of mixture at different ages are plotted. Examination of Fig. 4 shows that concretes prepared at lower w/cm experienced significantly higher compressive strength for the three ages studied. This corroborates the well-established relationship between compressive strength and w/cm suggested elsewhere [34]. This relationship states that the bonds within the hydrated cement paste are the governing factors that influence the strength of concrete. Furthermore, at low values of w/cm early development of strength is ensured by products of hydration of C_3S and C_2S, namely C–S–H, overlapping between adjacent cement particles, as a result, a less heterogeneous material as a final product develops due to the bonding of the interface between aggregates and cement paste.

All concretes containing FA, albeit to different degrees, experienced certain loss of strength. This reduction was especially significant in specimens prepared at lower w/cm and containing higher amounts of FA. However, this trend seems to be gradually offset by the long-term improvement in the strength attributed to the micropore refinement of the concrete matrix due to the pozzolanic activity between FA and the cement particles, as has been comprehensively stated in the literature [19–21].

A closer detailed analysis showed that the reduction in strength was more pronounced in 0.29 and 0.37 w/cm concretes containing 40% FA at 28 days and 1 year (see Fig. 4). Conversely, the decrease in strength in concretes containing higher amounts of FA and prepared at 0.45 w/cm were small at 28 days when compared to the control. Moreover, some of these specimens experienced higher values at 1 year and all of them were higher after 9 years. This confirms that at early ages the use of a high volume of fly ash has a physical rather than pozzolanic effect, that is, it acts as inert filler. In general, FA have a physical or filler effect on the fresh concrete mix due to its particle size distribution which are similar in range but not of the same size distribution as ordinary portland cement [35,36].

When CNI was added to the mixture, an increase in the compressive strength was observed in the majority of the mixtures. Specifically, concrete specimens containing 12.5 L/m^3 of CNI presented an increase in the strength of approximately 15% for all ages studied. Likewise, when 25 L/m^3 of CNI were used, neither a difference nor a slightly higher strength was observed in comparison with concretes containing 12.5 L/m^3; however, this positive effect in the strength was more pronounced in concretes prepared without fly ash for the three ages studied (see Fig. 4).

Perhaps the most encouraging result from the point of view of the HPC concrete is that the interaction of CNI with FA and silica fume does not adversely affect the short and long term compressive strength of concrete. Actually, an enhancement of the compressive strength at later ages was observed in concretes containing such combination, even after long-term exposure to a marine environment (Fig. 4). This is consistent with what was reported by Popovics [37] who concluded that the incorporation of certain chemical admixtures in concrete containing fly ash-silica fume combinations tends to enhance the compressive strength of mortars more than fly ash or silica fume alone. These findings, however, are the opposite of what was found by others [8] who

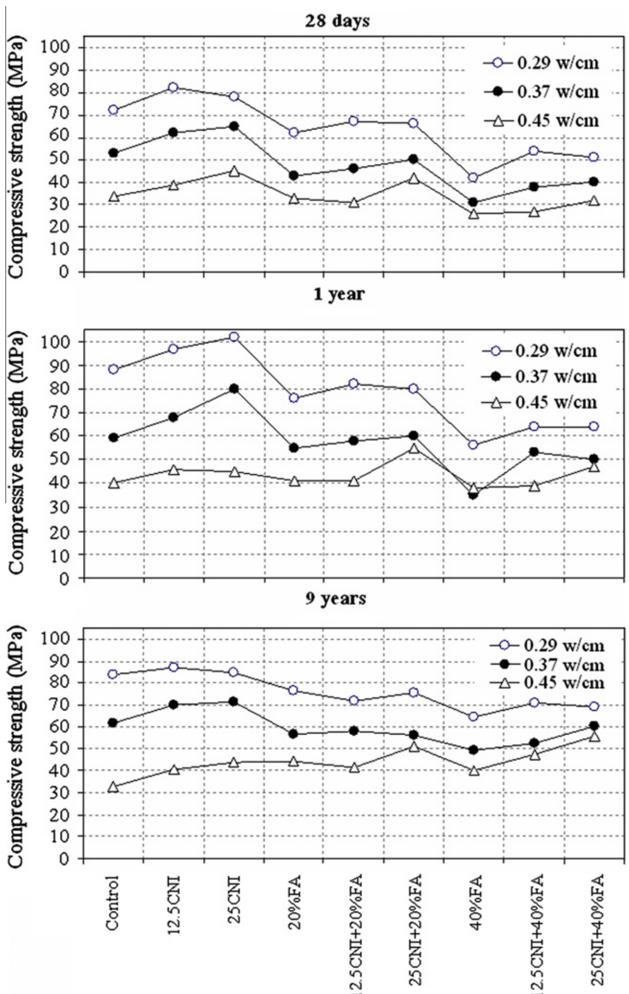

Fig. 4. Variation of compressive strength with type of mixture at different ages.

suggested that the incorporation of CNI into HPC tends to accelerate the formation of calcium hydroxide and ettringite crystals, and weakens the pore refinement effect caused by the secondary hydration reaction of FA and microsilica. In the same study, they also pointed out that the addition of CNI into concrete may also provoke negative effects on the porosity of cement paste, because when mixed in concrete CNI tend to increase the crystal quantity produced in the mixture, which leads to the increase of micropore volume and diameter. However, it has been recognized that in concretes prepared at very low values of w/cm, that is the case of HPC, porosity is not a governing factor on the compressive strength of concrete [34]. Moreover, the addition of FA tend to offset the negative effect that the use of CNI has in the porosity of concrete because its very fine particles serve as nucleation sites for internal hydration of cement products within the concrete pores, thus a finer pore structure is developed. This hypothesis has been corroborated by other reported studies [38–40] which have concluded that FA leaded to the enhancement in the pore refinement of the concrete micro-structure due to its fineness and to the predominantly spherical shape of its particles.

As observed by others [41,42], prolonging the curing period evidently enhances the compressive strength development of HPC concretes containing FA. This benefit is attributed to the fact that pozzolanic reaction between FA with the cementitious system is slow; hence, the enhancement of the compressive strength, due to the hydration of the cement particles and the refinement of capillary pores were exhibited at later ages [43]. From the testing results it was also observed that the curing conditions to which the concrete specimens were exposed played an important role in the long-term compressive strength development of HPC. While 1-year concrete cylinders were cured under standard laboratory conditions; the 9-year old concrete slabs, where the prismatic specimens were obtained, were field cured in sea water and subjected to harsh environmental conditions including wetting and drying cycles. Consequently, the expected enhancement in the compressive strength with the pozzolanic reaction of fly ash and silica fume in the 9-year old concrete may not be sufficiently developed due to these poorly-cured conditions. However, as depicted in Fig. 4, it was also observed that the addition of higher amounts of fly ash seems to minimize this negative effect in most of the 9-year old concrete specimens. These findings are in agreement with the results reported in a research program which evaluated the effects of curing conditions on the compressive strength of plain concrete specimens and those containing mineral admixtures [44]. They came to the conclusion that concrete prepared with mineral admixtures, under cyclic wetting and drying conditions in simulated seawater, exhibited higher strength loss compared to plain portland cement concretes cured under potable water.

Finally, it is recognized that in assessing the results from the current program, the geometrical difference between concrete cylinders, tested at 28 days and 1 year, versus the 9-year prismatic specimens obtained from the concrete slabs previously exposed to a marine environment, may have induced certain discrepancies on the values of compressive strength obtained at different ages, despite the appropriate procedures used for size and shape corrections. For this reason, the main objective of this research was not to correlate compressive strength values obtained at different ages, nor to quantify the effects of the exposure of concrete to a marine environment on the compressive strength, but rather to verify the occurrence or not of detrimental reactions between the constituents of the concrete on such property at different ages.

5. Conclusions

Based on the experimental results, the following conclusions can be drawn:

1. In this study, the influence of w/cm on the compressive strength of concrete containing fly ash and CNI was clearly demonstrated. In general, the lower the w/cm the higher the compressive strength.
2. When fly ash was used to replace portland cement blended with 8.2% silica fume, the compressive strength of the concrete at early ages decreased for most of the mixtures studied; however, at late ages the addition of higher amounts of fly ash was found to be beneficial.
3. The particle grading (physical aspect) of FA and 8% silica fume cement and their pozzolanic reactivity (chemical aspect), exerted significant influences on the short and long term compressive strength of concrete.
4. When CNI was added to the concrete mixtures, an increase in compressive strength of concrete containing fly ash was observed for all of the w/cm studied. Moreover, CNI tend to compensate for the reduction in compressive strength caused by the addition of fly ash.
5. The positive influence of CNI on the compressive strength of concrete was more evident in specimens prepared at 0.37 w/cm for the three ages studied either when it was used alone or in combination with fly ash.

6. After long-term exposure to a marine environment, concrete specimens containing CNI alone or in combination with FA showed similar or higher compressive strength values in excess of the 28-day moist-cured specimens, which is an indication of the stability and bond within the hydrated products of the cement paste.

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