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Diffusion of Chlorides in Pozzolanic Concrete made with High-absorption Aggregates Exposed under Tropical Marine Environment

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Due to the highly aggressive environment in the Caribbean coast, the housing infrastructure built in this region is continually affected, with heavy losses due to the electrochemical process of corrosion of the reinforcing steel embedded in concrete. In order to obtain a better understanding of the diffusion of chlorides in concrete made with highly-porous limestone, two types of cement were employed: ordinary Portland cement and pozzolanic cement. The aggregate employed was crushed limestone for both, coarse and fine aggregate (5% absorption). Two water to cementitious materials ratios were used: 0.5 and 0.7, equivalent to 35 and 20 MPa, respectively; and two curing treatments: 1-day and 14-day wet curing periods. Concrete specimens were prismatic, 15 by 15 by 20 cm. After two weeks of casting, concrete specimens were exposed to marine environment, at 90 m from the shoreline. Performance of the external concrete layer was determined by chloride ingress using an acid-soluble extraction method, followed by potentiometric titration with a silver ion-selective electrode. Results indicate that chloride concentrations were higher for the ordinary Portland cement specimens compared with the pozzolanic cement specimens, and high enough to onset corrosion of the reinforcing steel for the 0.7 w/cm OPC specimens after only 51 months of exposure.

Keywords: chloride concentration, concrete curing, limestone aggregate, marine environment, pozzolanic cement.

1. INTRODUCTION

The environment in the Gulf of Mexico coast is highly aggressive. As a result, reinforced concrete infrastructure in this region is continually affected with heavy losses due to corrosion of the reinforcing steel. This fact was confirmed in a previous research where several coastal developments were studied along the northern coast of the Yucatan peninsula [1, 2].

Under normal conditions, concrete surrounding the reinforcing steel provides enough protection, both physical and chemical, against the environment. Concrete supplies an alkaline environment, from the concrete pore solution, that surrounds the reinforcing steel allowing the formation of an oxide layer. This oxide layer is called the passive layer and protects the steel against corrosion.

Corrosion of the reinforcing steel occurs mainly by the destruction of the passive layer. In marine environment this may occur if enough amounts of chlorides reached the surface of the reinforcing steel, even if the concrete alkalinity is high.

Corrosion in this case is an electrochemical process in which corrosion cells are formed at the steel surface due to the concentration difference of the dissolved ions. Transformation of iron metal into ions and corrosion products is accompanied by a positive volume change compared to the original metal volume. This volume increment is the main cause of concrete cracking and spalling that can be observed in concrete constructions along the coast [1].

The Yucatan peninsula is characterized by a Karstic plateau; it has more than 1000 km of sandy, wide and flat beaches bathed by the sea from the Gulf of Mexico, in the north and west, and by the Caribbean Sea in the east; an inter-medium transition zone made of marshes runs parallel to the coast. From the geological point of view, the Yucatan peninsula is a unit formed by marine calcareous sediments from the Cenozoic era with uniformed morphological and structural characteristics. The age of formation of the limestone is in the range from the Eocene – Palaeocene until the Holocene – Pleistocene [3]. Therefore, limestone is the only source of aggregate for concrete construction in the peninsula, and due to its formation this limestone is highly porous. Due to its high porosity, this aggregate is doubtful as a suitable material to obtain concrete formulations that may withstand the harsh marine environment [4].

On the other hand, pozzolanic materials are increasingly used in cement formulations to improve concrete durability, especially in marine environments. In Nordic countries the use of 3 to 5 % of silica fume is mandatory for the case of severe environment. Also, the use of fly ash to reduce chloride ion ingress is common in concrete facilities under marine exposure. However, pozzolanic materials, including volcanic ash, are more prone to suffer from lack of curing, as most of them start to react at least two weeks after casting when the concrete pore solution is high enough to react with the pozzolans [5].

Thus, the objective of this investigation was to assess the combined effect of porous limestone aggregate and pozzolanic cement in the performance of concrete against chloride ingress under tropical marine environment.

2. METHODOLOGY

Concrete mix design followed the ACI procedure. Two types of cement were employed, ordinary Portland cement (OPC) and pozzolanic cement (PPC); both were commercially available. Two water-to-cementitious-materials (w/cm) ratios were employed, 0.5 and 0.7, in order to reach a compressive strength of 32.4 and 19.6 MPa, respectively. The former was chosen as the maximum w/cm allowable for durability purposes, and the latter was chosen to represent old construction practices based on compressive strength only. Thus, a matrix of 2 by 2 concrete mixtures was obtained. Also, two curing treatments were employed: 1-day and 14-day wet curing periods, the former to represent old construction practices and the former to allow the reaction of the pozzolanic material. In addition, control specimens for compressive strength were allowed full curing for 28 and 90 days. Curing was achieved by immersion in lime saturated water, except for the 1-day curing period which was achieved inside the molds. The fine and coarse aggregate employed was crushed limestone with at least 5% absorption (Table 1).

Table 1. Aggregate properties

Property	Coarse	Fine
Dry-rodded unit weight (kg/m^3)	1 298	--
Bulk specific gravity	2.38	2.48
Absorption (%)	5.34	5.04
Fineness modulus	--	3.11
Nominal maximum size (mm)	19	--

Three different concrete specimens were cast for compressive strength tests, porosity tests, and for chloride exposure. For compressive strength the specimens were cylindrical in shape, 100 mm in diameter by 200 mm high. For porosity tests the specimens were also cylindrical in shape, 75 mm in diameter by 150 mm high. For chloride exposure the specimens were prismatic in shape, 150 by 150 by 200 mm. A total of 12 concrete cylinders 200 mm high, 2 concrete cylinders 150 mm high, and 9 concrete prisms were cast per concrete mixture. Compressive strength tests were performed at 28 and 90 days in order to allow full pozzolanic hydration of the material in the control specimens that were allowed to cure until the day of testing.

After concrete specimens were two weeks old, they were exposed to marine environment, at 90 m from the shoreline. Performance of the external concrete layer was determined by chloride ingress at the beginning of the test, and after 6, 12, and 51 months of exposure. Two specimens were removed per concrete mixture each time of testing. Concrete dust was obtained at 10 mm intervals by drilling several holes up to 60 mm in each specimen, employing a one inch (25.4 mm) drill bit, although deeper holes were drilled after 51 months of exposure. The drilling machine was equipped with a vacuum system to collect the dust. After drilling, concrete dust was powdered to pass a sieve No. 50 (300µm). The Florida Department of Transportation (FDOT) method was employed for acid soluble chloride extraction [6]. After that, potentiometric titration with a silver ion-selective electrode was performed according to FDOT method to determine the chloride concentration.

3. RESULTS

Table 2 presents the results for the mixture design before daily moisture corrections. As the fine aggregate was also crushed limestone, it required more water to reach the desired workability.

Table 2. Mixture dosage per cubic meter

Materials	w/cm ratio	
	0.5	0.7
Cement (kg)	410	293
Water (kg)	205	205
Coarse aggregate (kg)	765	765
Fine aggregate (kg)	726	814

Table 3 presents the results for the fresh concrete. The unit weight was near the lower limit for regular weight concrete but it was expected due to the low bulk specific gravity of the aggregates employed. The slump was in the range for the desired workability (75 to 100 mm), and the air content was slightly above the expected 2 %.

Table 3. Fresh concrete properties

Mixture	Unit weight (kg/m$^{3)}$	Slump (mm)	Air content (%)
0.5 OPC	2 184	87	2.5
0.5 PPC	2 184	78	2.7
0.7 OPC	2 155	90	n. a.
0.7 PPC	2 174	82	3.0

Table 4 presents the results of the compressive strength tests performed after 28 and 90 days. There was no gain in compressive strength from 28 days to 90 days, which is expected in concrete elements cast under hot environments. Control specimens reached the expected values of 32.4 and 19.6 MPa for the 0.5 and 0.7 w/cm ratios, respectively. OPC specimens with 1-day curing reached at least 90% of the expected value, while specimens with 14-day curing reached beyond the expected value. All PPC specimens reached compressive strength values above the expected ones. PPC specimen’s compressive strength values ranged 7 to 35 % above OPC specimen’s values.

Table 4. Compressive strength tests (MPa)

Type of cement	w/cm 0.5 Curing treatment 1-day	 0.5 Curing treatment 14-day	 0.5 Curing treatment control	 0.7 Curing treatment 1-day	 0.7 Curing treatment 14-day	 0.7 Curing treatment control
@28 days						
OPC	29.7	38.9	32.9	20.2	25.5	22.1
PPC	38.3	43.2	40.0	25.9	33.4	29.2
@90 days						
OPC	29.1	36.4	34.9	19.1	27.5	22.7
PPC	35.0	39.1	39.8	23.9	33.0	30.8

Table 5 shows concrete porosity results after 90 days. Values were high, above 22%, although as expected due to the highly porous aggregate employed in the concrete mixture.

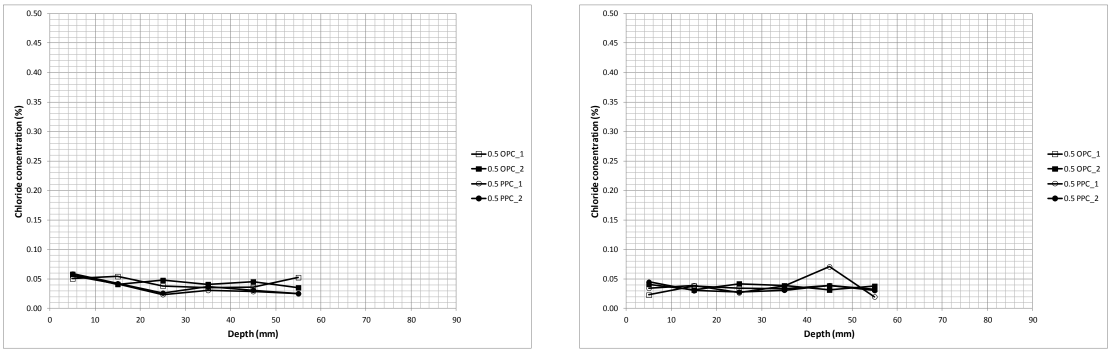
Table 5. Concrete porosity (%) after 90 days

Type of cement	w/cm 0.5	 0.7
OPC	22.7	25.4
PPC	23.9	24.7

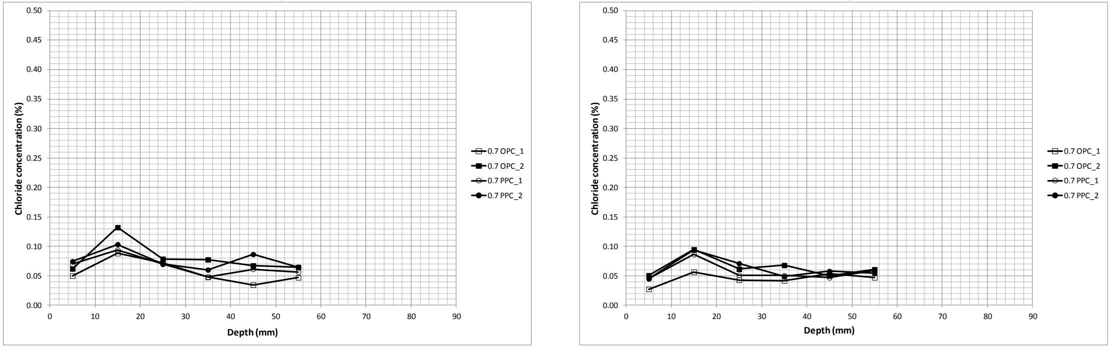
Figure 1 shows the results of the acid soluble chloride tests (FDOT) after 6 months of exposure which can be considered as the total chloride concentration. Higher chloride concentrations can be observed for the specimens with higher w/cm ratios. However, at this time there is no difference in chloride concentrations between the OPC specimens and the PPC ones, or between 14 days of curing and 1 day of curing for the same w/cm ratio.

Figure 2 shows the results of the acid soluble chloride tests (FDOT) after 12 months of exposure. At this time, it was observed again higher chloride concentrations for the specimens with higher w/cm ratios. For the 0.7 w/cm specimens, higher chloride concentrations are observed for the specimens with 1-day curing compared with the ones with 14-day curing. Also for the 0.7 w/cm specimens, higher chloride concentrations are observed for the OPC specimens than for the PPC ones. No clear tendencies can be observed from the 0.5 w/cm specimens for any curing treatment involved.

Figure 3 shows the results of the acid soluble chloride tests (FDOT) after 51 months of exposure. At this time, it was confirmed the previously observed behavior of higher chloride concentrations for the specimens with higher w/cm ratios. Also it was confirmed, for the 0.7 w/cm specimens, the previously observed higher chloride concentrations for the specimens with 1-day curing compared with the ones with 14-day curing as well as the higher chloride concentrations for the OPC specimens than for the PPC ones. As the chloride concentrations for the 0.7 w/cm specimens were still high at the previously deepest point tested, deeper holes were drilled in the concrete specimens. The high chloride concentrations were confirmed.

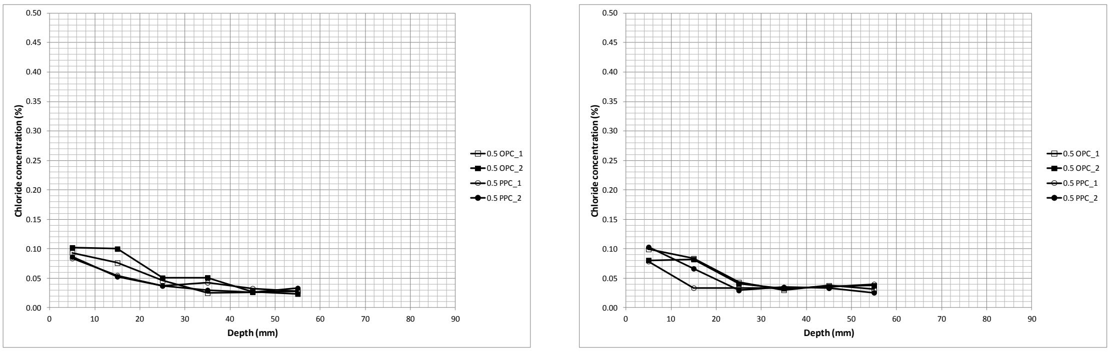


14-day curing, 0.5 w/cm 1-day curing, 0.5 w/cm

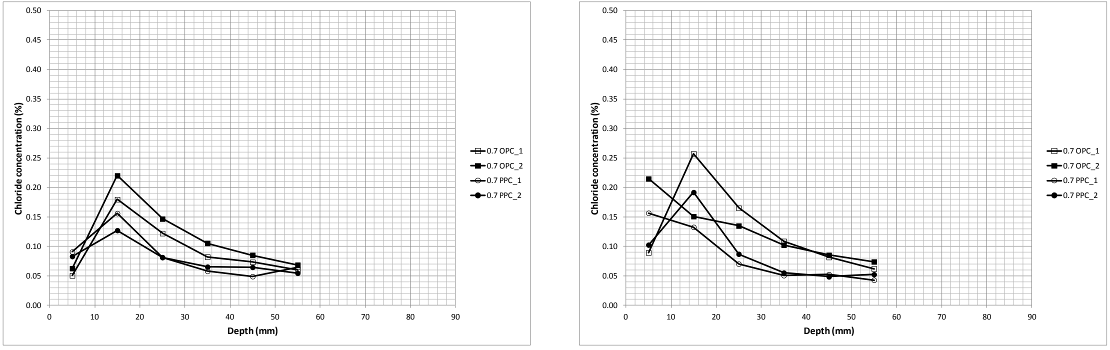


14-day curing, 0.7 w/cm 1-day curing, 0.7 w/cm

Figure 1. Total chloride concentration by weight percent of cement after 6 months

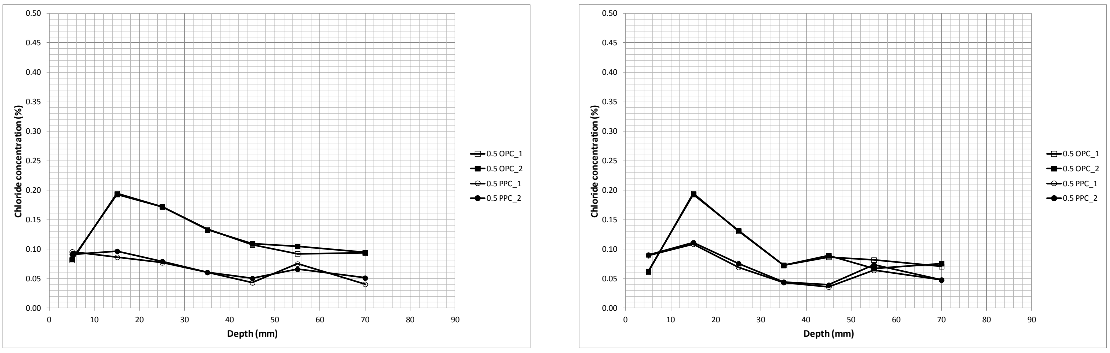


14-day curing, 0.5 w/cm 1-day curing, 0.5 w/cm

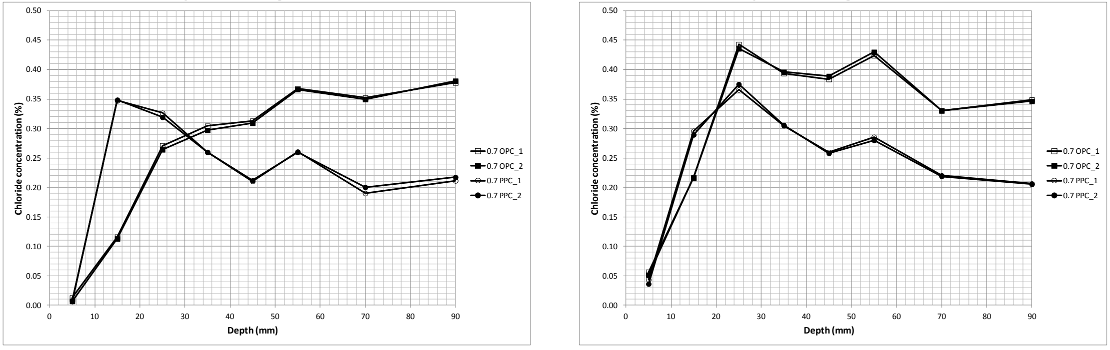


14-day curing, 0.7 w/cm 1-day curing, 0.7 w/cm

Figure 2. Total chloride concentration by weight percent of cement after 12 months



14-day curing, 0.5 w/cm 1-day curing, 0.5 w/cm



14-day curing, 0.7 w/cm 1-day curing, 0.7 w/cm

Figure 3. Total chloride concentration by weight percent of cement after 51 months

For the 0.5 w/cm specimens, higher chloride concentrations were observed for the OPC specimens than for the PPC ones, although no differences were observed between the curing treatments involved. Chloride concentrations for the 1-day curing OPC 0.7 w/cm were high enough to cause corrosion onset of reinforcing steel.

4. DISCUSSION

Due to the high temperatures in the tropical environment (>25ºC), hydration proceeded as expected in a hot environment resulting in high gain in compressive strength at the beginning with no gain after 28 days of casting. This allowed a better hydration of the pozzolanic cement. As a result, PPC specimens reached compressive strength values higher than the OPC specimens.

Even though the concrete specimens from both w/cm presented a very high porosity (from 22 to 26%), there was a difference in the chloride concentrations between 0.5 and 0.7 w/cm. Thus suggesting that total concrete porosity is not a good criterion to qualify concrete for durability purposes, at least when employing high absorption aggregates.

Chloride diffusion coefficients using Fick's second law were obtained after 12 and 51 months of exposure to the marine environment. These coefficients are presented in Table 6. The average diffusion coefficients in PPC specimens are lower than those in OPC specimens for both w/cm ratios, although the difference is greater for 0.7 w/cm. To prove if the differences were significant, a Mann-Whitney non parametric analysis was performed for the diffusion coefficients obtained after 12 months. It was found that there was a significant difference for both, the 0.5 and the 0.7 w/cm diffusion coefficients. However, at this point, there is no difference between the curing treatments employed after 51 months of exposure to the marine environment.

Table 7 presents the chloride diffusion coefficients from several researchers from other parts of the world. Mangat and Gurusamy [7] studied concrete specimens with and without cracks exposed to wet and dry cycles in lab and marine environments between 3 months and 5 years. Liam et al. [8] studied a 24-year old concrete jetty in a tropical marine environment. Andrade et al. [9] studied concrete specimens with OPC and fly ash exposed to 3 Molar NaCl solution for 35 days. Mohammed et al. [10] employed concrete specimens with OPC and fly ash exposed to wet and dry cycles with sea water.

Table 6. Chloride diffusion coefficients after 12 and 51 months of exposure

Specimen	Diffusion coefficient @ 12 months (cm^2/s)	Diffusion coefficient @ 51 months (cm^2/s)
0.5 OPC 14-day	1.05×10^{-7}	1.01×10^{-7}
0.5 OPC 1-day	1.21×10^{-7}	0.57×10^{-7}
0.5 PPC 14-day	0.52×10^{-7}	0.48×10^{-7}
0.5 PPC 1-day	0.30×10^{-7}	0.21×10^{-7}
0.7 OPC 14-day	1.41×10^{-7}	--
0.7 OPC 1-day	2.08×10^{-7}	--
0.7 PPC 14-day	0.72×10^{-7}	1.80×10^{-7}
0.7 PPC 1-day	0.76×10^{-7}	1.83×10^{-7}

The results from this investigation for 0.5 w/cm ranged from 0.21 to 1.01 x 10^{-7} cm^2/s. These results are in the same range than those results from other researchers for similar concrete qualities (Table 7). Therefore, sufficient concrete quality can be obtained despite the use of the highly-porous limestone aggregate, although better results were obtained with puzzolanic cement as opposed to OPC.

Table 7. Chloride diffusion coefficients from other investigations

Researcher	Diffusion coefficient (1×10^{-7} cm^2/s)	w/cm
Mangat & Gurusamy [7]	0.20 to 0.75	0.40
Liam et al. [8]	0.33 to 0.55	0.50
Andrade et al. [9]	0.17 to 0.54	0.40
Mohammed et al. [10]	0.22 to 0.52	0.45
Castro & Maldonado [11]	0.70 to 1.10	0.46
Jiménez & Moreno [12]	0.21 to 0.38	0.50

These results differed from the results of a previous research with similar materials and the same exposure environment [11]. In that study, diffusion coefficients in the range of 0.7 to 1.1 x 10^{-7} cm^2/s were obtained for 0.46 w/c cylindrical specimens (150 mm high, 75 mm diameter) exposed at 50 m from the shoreline. The difference may be attributed to the corner effect and the small size of the specimens that resulted in higher apparent diffusion coefficients than the ones obtained in the present work. On the contrary, in a recent work [12] with similar materials but with ten-week synthetic sea water exposure, diffusion coefficients in the range 0.2 to 0.4 x 10^{-7} cm^2/s were obtained from the wet-dry section for the OPC 0.5 w/c prismatic specimens (100 mm by 150 mm by 600 mm) and 1.57 to 1.82 x 10^{-7} cm^2/s were obtained for the 0.7 w/c ones. In both cases these values correlate well with the ones from this investigation lending support to the fact that sufficient concrete quality can be obtained even with the use of the highly-porous limestone aggregate as long as a low w/c is employed.

5. CONCLUSIONS

Chloride concentrations were significant higher for the ordinary Portland cement specimens compared with the pozzolanic cement specimens. Chloride concentrations for the 0.7 w/cm OPC were high enough to cause corrosion onset of reinforcing steel after only 51 months.

In the case of concrete mixtures, durability design (low w/cm) prevailed over strength-only design (high w/cm) when exposed to marine environment.

Diffusion coefficients for chloride in concrete made with high-absorption aggregate were in the same range compared to other results made with different materials from all around.

Good concrete quality can be obtained despite the use of the highly-porous crushed limestone aggregate, although better results were obtained with puzzolanic cement as opposed to OPC.

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