

Accelerated Carbonation of Concrete Specimens Employing High-Absorption Limestone Aggregate

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ABSTRACT

Besides chlorides, concrete carbonation may promote corrosion of the reinforcing steel in concrete. In urban tropical locations, away from the marine environment, carbonation may be the single cause of corrosion in reinforced concrete elements. Previous investigations in reinforced concrete buildings have showed significant concrete carbonation after only 20 years of service. As lower mechanical strength is required for concrete elements involved in housing construction than that required for concrete buildings, faster carbonation rates are expected in concrete houses than those observed in concrete buildings. This investigation is aimed at the impact of carbonation in concrete elements used for building and housing construction. Four different water/cement ratios were used employing high absorption limestone aggregate. Plain and reinforced concrete specimens were exposed in a 4% carbon dioxide chamber at 60% relative humidity. After full carbonation, reinforced concrete specimens were transferred to a 95% relative humidity chamber. The corrosion behavior was monitored using a linear polarization resistance technique. Results indicate that the lower the water/cement ratio the lower the carbonation rate despite the high concrete porosity observed in all concrete mixtures due to the use of high absorption limestone aggregate. Estimates of the length of the corrosion initiation period based on the measured carbonation coefficients are presented.

KEYWORDS

Accelerated tests, Carbonation, Corrosion, Limestone aggregate, Reinforced concrete.

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1 INTRODUCTION

Reinforcing steel is protected in concrete structures from the atmospheric environment due to the high alkaline environment provided by the pore solution ($\text{pH} > 12.5$ units). However, it may corrode if this protection is lost. The protection may be lost due to the neutralization of the concrete pore solution surrounding the reinforcing steel. This neutralization of the pore solution is also called concrete carbonation. Concrete carbonation is the result of the reaction of hydrated cement compounds with atmospheric CO_2 . Carbonation reduces the pH of the concrete pore solution ($\text{pH} \approx 8$ units), developing uniform corrosion in the reinforcing steel. This uniform carbonation-induced corrosion accelerates the crack formation if the right conditions of temperature and humidity are present. In places with tropical climate, atmospheric conditions may encourage the carbon dioxide aggressiveness due to high humidities and temperature [Veleva *et al.* 1998]. Carbonation rate depends on several factors [Bakker 1988], such as the type and amount of cement, porosity of the material, type and amount of pozzolanic additions, etc. [Moreno 1999, Moreno & Sagüés 1998].

Previous investigations in reinforced concrete buildings made with high absorption limestone aggregate have showed significant concrete carbonation after only 20 years of service [Castro *et al.* 1999, Moreno *et al.* 2002]. Those concrete buildings, with compressive strength values in the range of 20 to 30 MPa, had carbonation coefficients in the range 5 to 8 $\text{mm/year}^{1/2}$. According to the literature, more than 6 $\text{mm/year}^{1/2}$ indicates a bad quality concrete [Ho & Lewis 1987].

Another indication of concrete quality is the value of the porosity of concrete. The porosity results obtained in those concrete buildings ranged from 18.6% to 30.4% [Castro *et al.* 1999, Moreno *et al.* 2002]. According to the literature [Troconis-Rincón *et al.* 2000], values exceeding 15% of porosity are considered bad quality concrete. These high porosity values are attributed to the high absorption limestone aggregate employed.

The question remains whether good quality concrete can be obtained with the use of high absorption limestone aggregate. Therefore, this investigation is aimed at the impact of carbonation in reinforced concrete elements with high absorption limestone aggregates used for building and housing construction.

2 METHODOLOGY

2.1 Specimens and Materials

Four different concrete specimens were used. Instrumented concrete prisms 50 mm by 100 mm by 200 mm were used to monitor the corrosion process. They were reinforced with two corrugated steel bars (rebars #3), 9.5 mm in diameter, and an internal reference electrode made of activated titanium rod covered with mix-metal oxide (ATR) was placed in the middle of each specimen [Castro *et al.* 1996]. Specimens were prepared in triplicate (Fig. 1). In addition, plain concrete cylinders 150 mm by 75 mm diameter were used to monitor the carbonation progress. Plain concrete cylinders 50 mm by 100 mm diameter were used for porosity measurements and plain concrete cylinders 300 mm by 150 mm diameter were used for compressive strength determinations.

Four water/cement ratios were used (0.8, 0.7, 0.62, and 0.55, that correspond to 15, 20, 25, and 30 MPa). The cementitious material was Ordinary Portland Cement with no mineral additions. Crushed limestone was used as coarse and fine aggregate, with absorptions of 5.5 and 4.7 %, respectively [ASTM C 642 2004]. Mixture designs were prepared according to ACI specifications [ACI 211 1997] and the specimens were cast following ASTM standard procedures [ASTM C 192 2002]. Concrete specimens were cured by immersion in lime saturated water for 15 days.

As carbonation proceeds a slow rate, a carbonation chamber was set up to accelerate the process. To ensure enough maturity at the time of the accelerated test, the specimens were allowed to condition at the lab environment for 80 days as a pretreatment and then exposed to a 4% CO₂ environment (~60% RH) in the carbonation chamber for ~100 days, except for mixture 0.55 that was exposed for longer time (176 days) to ensure complete carbonation.

After carbonation, the instrumented specimens were placed in a moisturizing chamber (>90% RH) to increase the corrosion rates.

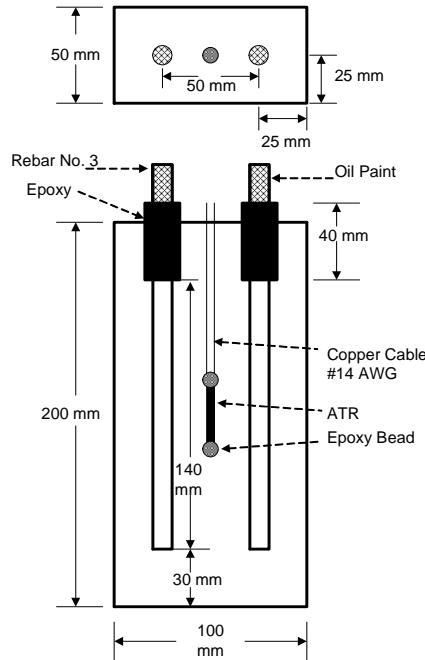


Figure 1. Sketch of the reinforced concrete specimens.

2.2 Porosity Measurements

Two concrete specimens were employed per mixture design to measure concrete porosity. Measurements were performed according to ASTM C 642 [2004]. Acceptance criteria are less than 10% is considered good quality concrete, more than 15% means bad quality concrete [Troconis-Rincón *et al.* 2000].

2.3 Compressive Strength Measurements

Three concrete specimens were employed per mixture design to measure compressive strength. Measurements were performed according to ASTM C 39 [2004].

2.4 Carbonation Depth Measurements

Two plain concrete specimens per mixture design were removed from the carbonation chamber at different times. A ~50 mm slice was split from each specimen and a 1% phenolphthalein solution was sprayed on top of the broken surfaces following the RILEM criteria [CPC-18 1988]. Non-carbonated concrete reacted with the phenolphthalein solution showing a dark pink color. Carbonated concrete remained colorless. Carbonation depth was measured at eight different points using a caliper. Each measurement was corrected from radial measurements in a cylinder into carbonation depth measurements that would be obtained in a semi-infinite plane [Moreno 1999]. Once corrected, the average was obtained for each cylinder, and the result was averaged with the result from the other concrete specimen, obtaining an average from each pair of specimens. After that, carbonation

coefficient was estimated using the time of accelerated exposure and corrected for the initial carbonation occurred during the conditioning period [Moreno *et al.* 2007]. Acceptance criteria are less than 3 mm/year^{1/2} is considered good quality concrete, more than 6 mm/year^{1/2} means bad quality concrete [Ho & Lewis 1987]. After taken the carbonation measurements, the remaining portion of the non-instrumented concrete cylinders were placed back in the carbonation chamber.

2.5 Half Cell Potentials

Half cell potentials were measured for each rebar against the internal reference electrode during the carbonation period after calibration against an external copper-copper sulfate electrode placed on the external concrete surface. Corrosion criteria used was that of the literature [Troconis-Rincón *et al.* 2000].

2.6 Concrete Electrical Resistance

Electrical resistance of the concrete was monitored using an AC electrical resistance meter with a Wenner probe. The electrical resistance was measured from one rebar to the other using a two point array.

2.7 Corrosion Rates

Linear polarization resistance tests using a potentiostat were performed during the carbonation and the moisturizing periods without removing the specimens from the chambers. The tests were conducted starting from the open circuit value in the negative direction (-10 mV), to minimize possible capacitive effects, at a scan rate of 0.01 mV·s⁻¹ [Sagüés *et al.* 1997]. One rebar (X-bar) was always used as working electrode (WE), the other rebar (Y-bar) was used as counter electrode (CE). Corrosion rates were obtained multiplying 26 mV by the inverse of the polarization resistance from the test. Acceptance criteria are, less than 0.1 µA/cm² is considered meaningless corrosion, more than 0.5 µA/cm² means active corrosion [Troconis-Rincón *et al.* 2000].

3 RESULTS AND DISCUSSION

Table 1 shows the average results of compressive strength and porosity values obtained from the tests. Compressive strength values were above the design compressive strength. Density was in the range for normal concrete although close to the lower limit. Absorption and porosity were high but as expected based on the absorption values of the aggregates employed. According to the mentioned criteria, these porosity values would qualify the concrete mixtures as of bad quality, even for the low water/cement ratio of 0.55.

Table 1. Average compressive strength, absorption, porosity and density of concrete mixtures.

Mixture	Compressive strength (MPa)	Absorption (%)	Porosity (%)	Density
0.80	18.0	10.1	23.4	2.27
0.70	21.7	12.9	23.1	2.24
0.62	26.1	11.9	24.1	2.23
0.55	30.9	12.2	22.9	2.23

Table 2 shows the results from the carbonation depth measurements. Concrete specimens were fully carbonated when the carbonation depth was 37.5 mm. Due to the fact that mixture 0.55 was a better mixture than the others, carbonation depth was not determined at 51 days but at 112 days, instead. By day 51, mixtures 0.7 and 0.8 were fully carbonated.

Table 2. Carbonation depth measurements and standard deviations (mm).

Mixture	Days of exposure at 4% CO ₂			
	15	37	51	112
0.80	15.7	1.0	37.5	--
0.70	13.7	1.6	24.2	1.4
0.62	10.8	1.3	20.2	1.3
0.55	7.8	1.2	14.6	1.4
			n.a.	22.3
				1.3

Table 3 shows the carbonation coefficients at 4% CO₂ environment. Each coefficient was obtained from day 0. As the test is destructive in nature and different specimens were employed in each test, an average was calculated in order to minimize the experimental error. The higher the water/cement ratio of the mixture, the higher the carbonation coefficient. Therefore, there is a correlation between the water/cement ratio and the carbonation coefficient, despite the high porosity of all mixtures.

Table 3. Carbonation coefficients at 4% CO₂ exposure (mm/year^{1/2}).

Mixture	Days of exposure at 4% CO ₂				Average
	15	37	51	112	
0.80	77.0	--	--	--	77.0
0.70	68.0	83.5	--	--	75.8
0.62	54.0	71.2	57.0	n.a.	61.7
0.55	39.1	51.7	n.a.	42.8	44.5

Table 4 shows the carbonation coefficients transformed to ambient CO₂ exposure (about 400ppm), following the procedure published elsewhere [Moreno *et al.* 2007]. According to the literature, concrete mixtures 0.80, 0.70, and 0.62 should be considered of low quality. Concrete mixture 0.55 should be considered medium quality concrete; also, it is consistent with previous results employing a 0.50 mixture made with river rock as aggregate (K equal to 4.2 mm/year^{1/2}) [Moreno 1999].

Table 4. Transformed carbonation coefficients at ambient CO₂ exposure (mm/year^{1/2}).

Mixture	K _{4%CO₂}	K _{0.04%CO₂}
0.80	77.0	8.4
0.70	75.8	8.2
0.62	61.7	6.7
0.55	44.5	4.8

Assuming a concrete cover of 25 mm and 19 mm diameter reinforcing steel, 30 mm could be considered as average carbonation depth for active corrosion. Thus, the end of initiation time for active corrosion may be reached after 14 years for mixtures 0.80 and 0.70, 20 years for mixture 0.62, and 39 years for mixture 0.55. The estimated 14 and 20 years for corrosion initiation are consistent with the previous results from concrete buildings [Castro *et al.* 1999, Moreno *et al.* 2002].

Figure 2 shows the average potentials as a function of time. Potentials from mixtures 0.8, 0.7, and 0.62 showed a transition of more than 300 mV toward more negative values after 20 days of exposure. Mixture 0.55 has a less pronounced potential change after 70 days of exposure.

After moving the specimens to the humidity chamber, the potentials dropped ~150 mV in the less positive direction. The potentials tended to stabilize in the range -500 to -600 mV, which is the expected range for steel in concrete under active corrosion.

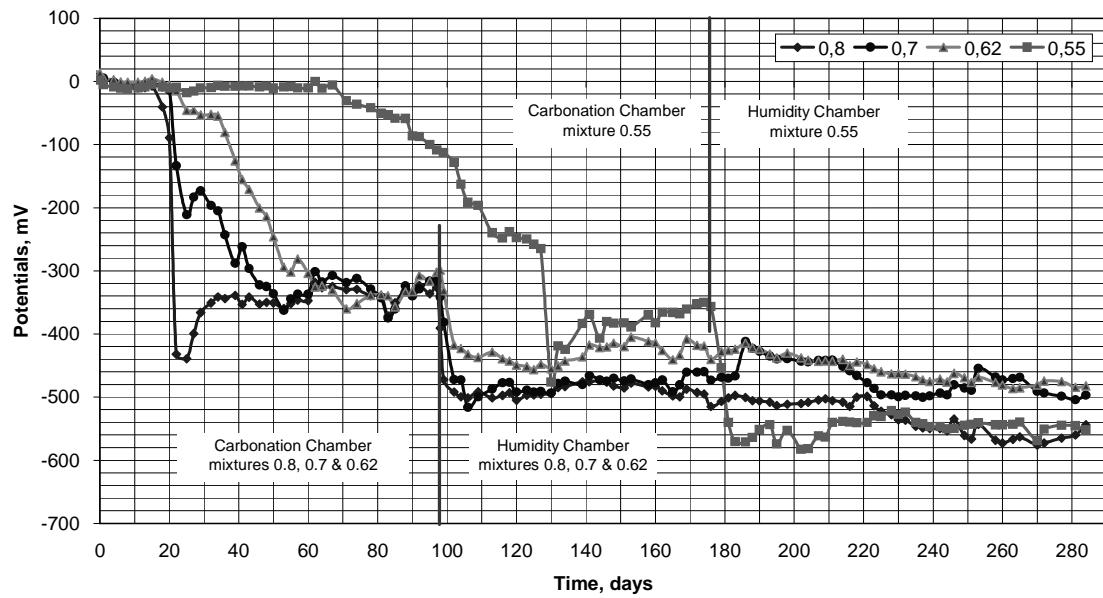


Figure 2. Average potentials as a function of exposure time.

Figure 3 shows the average concrete resistance with time. As the carbonation proceeded, the electrical resistance increased. However, once in the humidity chamber, the resistances dropped to very low values. It is noticeable that the final values were inversely correlated with the water/cement ratio; the higher the water/cement ratio, the lower the concrete resistance.

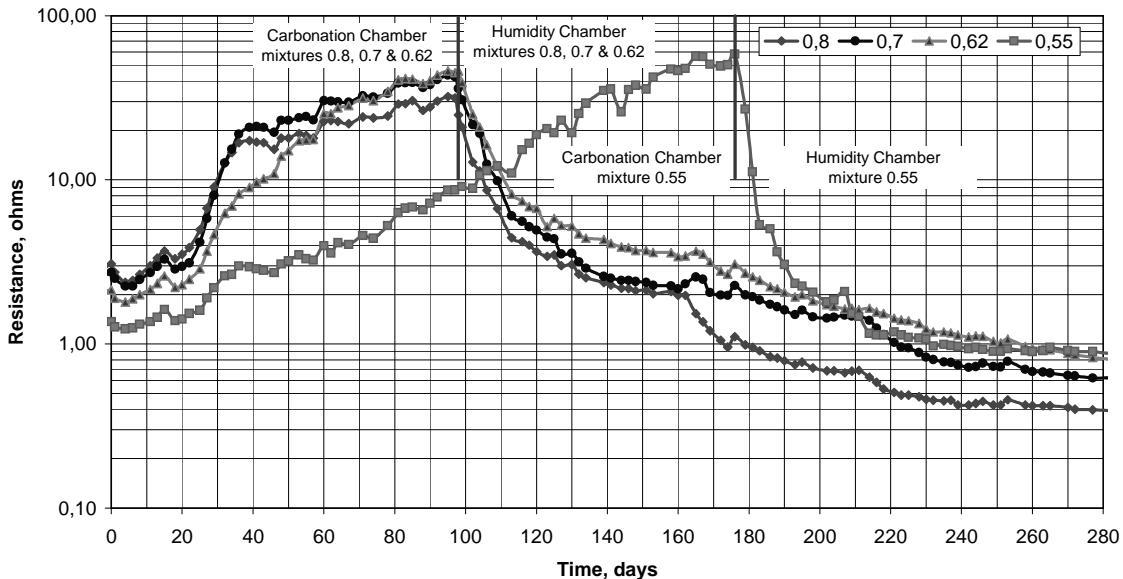


Figure 3. Average concrete resistance as a function of exposure time.

The apparent corrosion rates are presented in Fig. 4. As observed in previous investigations, corrosion rates during the accelerated carbonation period were very low. It is only after the specimens were moisturized than the onset of corrosion developed and active corrosion rates were achieved. As opposed to the electrical values, corrosion rates were directly correlated with the water/cement ratio; the higher the water/cement ratio, the higher the final corrosion rate. Extremely high corrosion rates above $1 \mu\text{A}/\text{cm}^2$ were recorded only for the highest water/cement ratio of 0.8. According to the literature, if constant this value would be enough to crack the concrete cover after only 2 years; again, this estimate is consistent with the previous results from concrete buildings [Castro *et al.* 1999, Moreno *et al.* 2002].

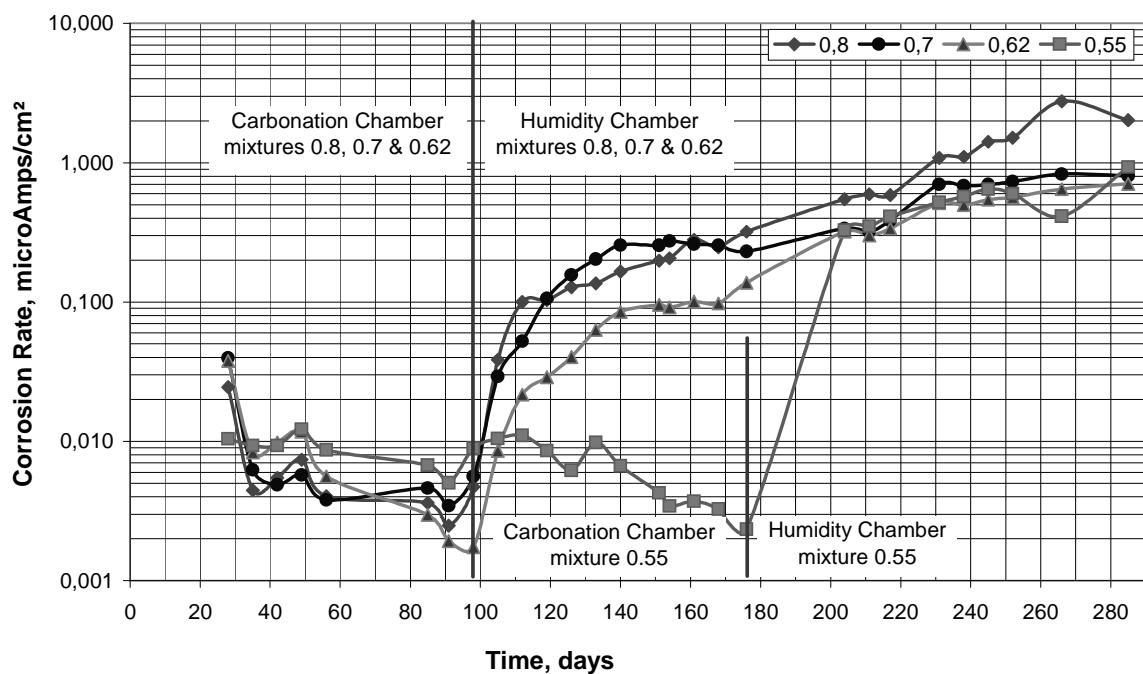


Figure 4. Average corrosion rates as a function of exposure time.

4 CONCLUSIONS

- The lower the water/cement ratio the lower the carbonation rate despite the high concrete porosity.
- Highest corrosion rates were observed at the highest water/cement ratio.
- Good quality concrete may be obtained even when using crushed limestone aggregate of high absorption.

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REFERENCES

ACI 211.1-91 1997, *Standard Practice for Selecting Proportions for Normal Heavyweight, and Mass Concrete*, ACI International, Farmington Hills, MI.

ASTM C 39-03 2004, *Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens*, ASTM International, West Conshohocken, PA.

ASTM C 192-98 2002, *Standard Practice for Making and Curing Concrete Test Specimens in the Laboratory*, ASTM International, West Conshohocken, PA.

ASTM C 642-97 2004, *Standard Test Method for Density, Absorption, and Voids in Hardened Concrete*, ASTM International, West Conshohocken, PA.

Baker, R. F. M. 1988, 'Initiation period', in *Corrosion of Steel in Concrete*, ed. P. Schiessl, Chapman and Hall, London, UK, p. 22.

Castro, P., Sagüés, A. A., Moreno, E. I., Maldonado, L., Genescá, J. 1996, 'Characterization of Activated Titanium Solid Reference Electrodes for Corrosion Testing of Steel in Concrete', *Corrosion*, **52**[8], 609-617.

Castro, P., Moreno, E. I., Genescá, J. 1999, 'Carbonation-induced corrosion of concrete coastal buildings in the north of Yucatan, Mexico', CORROSION/99, paper no. 565, NACE International, Houston, TX.

Ho, D.W., Lewis, R. K., 'The water sorptivity of concretes: The influence of constituents under curing', *Durability of Building Materials*, **4**, 241-252.

Moreno, E. I. 1999, *Carbonation of Blended Cement Concretes*, Ph.D. dissertation, University of South Florida.

Moreno, E. I., Sagüés, A. A. 1998, 'Carbonation-induced corrosion on blended-cement concrete mix designs for highway structures', CORROSION/98, paper no. 636, NACE International, Houston, TX.

Moreno, E. I., Castro, P., Leal-Murguia, J. 2002, 'Carbonation-induced corrosion of urban concrete buildings in Yucatan, Mexico', CORROSION/2002, paper no. 220, NACE International, Houston, TX.

Moreno, E.I., Solís-Carcaño, R. G., Serrano-Ixtepan, D., Arias-Palma, C. A. 2007, 'Performance of concrete coatings against carbonation-induced corrosion', NACE Corrosion/2007, Paper 07297.

RILEM Recommendations CPC-18 1988, 'Measurement of hardened concrete carbonation depth', *Materials and Structures*, **21**, 453-455.

Sagüés, A. A., Kranc, S. C., Moreno, E. I. 1995, 'Time Domain Response of a Corroding System with Constant Phase Angle Interfacial Component: Application to Steel in Concrete', *Corrosion Science*, **37**[7], 1097-1113.

Trocónis-Rincón, O., Romero-Carruyo, A., Andrade, C., Helene, P., Díaz, I. 2000, *Manual for Inspecting, Evaluating and Diagnosing Corrosion in Reinforced Concrete Structures*, CYTED, Maracaibo, Venezuela.

Vélela, L., Castro, P., Hernández-Duque, G., Schorr, M. 1998, 'The corrosion performance of steel and reinforced concrete in a tropical humid climate. A review', *Corrosion Reviews*, **16**[3], 235-284.