

Concrete carbonation and chloride penetration in a marine environment

A. Costa and J. Appleton

Instituto Superior Técnico, Technical University of Lisbon, Portugal.

ABSTRACT

In an inspection and appraisal study of a series of 25-year-old concrete structures in a dockyard constructed with poor quality concrete, it was found that both chloride penetration and carbonation played a significant role in the deterioration of the structures exposed to the marine atmospheric zone. This behaviour is unexpected as chloride penetration in this environment generally occurs more rapidly than carbon dioxide penetration.

This paper describes an experimental study conducted on the western coast of Portugal in order to evaluate the significance of the carbonation of concrete in a marine environment. A number of concrete slabs were exposed to a variety of marine environment conditions, and the carbonation depth and chloride penetration were measured over a period of six years. The long-term penetration of these two aggressive agents was evaluated on the basis of the experimental results obtained. It was concluded that if good quality concrete was used with an adequate concrete cover thickness to protect the reinforcement from the effect of chlorides, there would be a guarantee that carbonation would account for the deterioration of only a small part of the concrete cover layer, during the service life of the structures.

1. INTRODUCTION

The marine environment provides a highly aggressive exposure condition for reinforced concrete structures. Experience has shown that the deterioration mechanism of greatest significance in this environment is corrosion of reinforcement. This mechanism results in cracking and delamination of the concrete cover, and in the reduction of the cross section of the reinforcement which can seriously affect the load bearing capacity of structural elements.

There are various examples of structures on the Portuguese coastal strip that show a marked deteriora-

tion during the 5 to 10 years following construction [1, 2]. This fact is also reflected in the considerable costs involved in the repair of the deteriorated structures.

The onset of corrosion is either caused by the carbonation of the concrete cover or by the penetration of chlorides to the reinforcement level. In certain exposure conditions the combined action of these two aggressive agents can occur. In a marine environment, namely in the atmospheric zone, in the spray zone and in other areas in which the concrete has a low moisture content, this combined action can be of some significance.

In the marine atmospheric zone, concrete is never directly in contact with sea water but it is exposed to the effect of airborne chlorides carried by the sea wind. In the spray zone, concrete is exposed to spray created by the action of wind on waves.

Various studies [3-6] indicate that the interactive effects of carbonation and chlorides lead to a faster corrosion rate of the reinforcement. This effect fundamentally involves the instability of chloroaluminates in the presence of carbon dioxide, which gives rise to the decomposition thereof, with the subsequent release of chlorides into the concrete pore solution. Another study [7] of carbonation conducted in Kuwait concluded that, in structures located on the coast, carbonation occurs more rapidly than in structures located further inland.

A detailed study was carried out in 1996 in order to evaluate the deterioration of structures in a large dockyard built in 1973-75, located on the west coast of Portugal. The dockyard includes three large docks, 5 piers and various shipbuilding and repair support structures. Five years after construction, there were signs of marked deterioration on one of the docks caused by chloride induced corrosion. This deterioration started to gradually spread to all structures in contact with sea water (docks and piers). In these structures, the concrete at the

reinforcement level was deeply contaminated by chlorides. The carbonation depth was less than the concrete cover. At the present time, all structures have been or are being repaired. Approximately 50,000 m² of docks and 17,000 m² of piers have been repaired.

Structures exposed to the marine atmospheric zone showed a slower rate of deterioration. To date, significant areas of delamination of the concrete covering, caused by corrosion of the reinforcement have been observed in these structures. An assessment of these structures showed that the corrosion of the reinforcement was caused both by the penetration of chlorides and the carbonation of the concrete. The carbonation depth, measured on uncracked areas, generally varied from 20 to 50 mm, and in some zones, exceeded the chloride penetration depth.

The main cause of the deterioration of the structures was the poor quality of the concrete. The composition of the concrete used was as follows: cement content – 300 kg/m³; water-cement ratio – 0.70. The cube strength of the concrete is in the order of 20 MPa.

This paper presents the results of an experimental study in which carbonation and chloride penetration were evaluated in concrete slabs with various mix compositions subjected to a variety of marine environment exposure conditions, so as to analyse the significance of carbonation in this type of environment.

This research is part of a broader experimental study regarding the durability of reinforced concrete structures in marine environment [8].

2. EXPERIMENTAL WORK

2.1 Materials and concrete mixes

Three concrete mixes were studied, two for cast-in-situ and one for shotcrete. Portland cement CE I 32.5 was used in all mixes. Two limestone aggregates with a maximum size of 19.1 mm (aggregate I) and 9.5 mm (aggregate II), and a siliceous sand were used in cast-in-situ concrete C1 and C2. A superplasticiser was used in the concrete mix C2. Only a fine limestone aggregate (aggregate III) with a maximum size of 4.76 mm was used in the shotcrete. Microsilica and a superplasticiser were added to the shotcrete mix.

Mix type	C1	C2	C3
Cement, kg/m ³	300	425	500
Sand, kg/m ³	822	677	
Aggregate I, kg/m ³	500	481	
Aggregate II, kg/m ³	631	750	
Aggregate III, kg/m ³			1 704
Microsilica, kg/m ³			21.5
Superplasticiser, kg/m ³		10.2	
W/C ratio	0.5	0.3	0.35*
Slump, mm	70	170	
Dry density, kg/dm ³	2.33	2.41	2.32
Compressive strength, MPa	34	54	66

* average

Table 1 shows the composition and properties of the mixes used. The mix of shotcrete C3 relates to the shotcrete after it has been applied, *i.e.* after rebound losses.

Fifty-four concrete slabs measuring 1 x 0.5 x 0.12 m were cast and subjected to a humid cure for 7 days. All faces of the test slabs, except the upper face, were protected with an epoxy paint, so that carbonation and chloride penetration would only occur on that face. After two weeks, the slabs were subjected to a variety of marine environment exposure conditions. The exposure period was initiated in 1992.

2.2 Exposure conditions

The site chosen to expose the test slabs was the naval complex of Setenave, on the estuary of the river Sado, near Setúbal.

Here the environment is the typical temperate climate marine environment. The main climatic characteristics during the 1974-1990 period, are indicated in Table 2.

	Annual average	Day average
Air temperature	+ 16.8 °C	+ 11.1 °C (Jan) + 22.2 °C (Jul)
Relative humidity	78 % (9 h) 64 % (15 h)	Jan 89% (9 h) 73% (15 h) Jul 68 % (9 h) 54% (15 h)
Rain	538.6 mm	72.4 mm (Jan) 5.4 mm (Jul)
Evaporation	1505.4 mm	66.6 mm (Jan) 203.2 mm (Jul)

The measurement of the rate at which chlorides are deposited, measured over a year in accordance with ISO DP 9225 standard [9], produced the results in Table 3.

Month	Jan	Fev	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
Chloride [mg/m ² /day]	262	42.9	78.9	21	36	15.8	20.3	26.7	22.6	37.3	157	95.7

The chloride content of the estuary waters varies from 16 to 21 g/l during the year, according to the flow rate of the river Sado.

The concrete slabs were exposed at various locations in the dockyard and to different environmental conditions. The exposure conditions selected for this study were as follows:

A – Spray zone. This zone is subject to spray caused by the breaking of the waves, when the sea is rough.

B – The zone within dock 20. This site is subject to infrequent cycles of the filling of the dock with estuary water. After placing the slabs, they were subject to 30 cycles of filling and emptying over six years.

C – Atmospheric zone. This area is exposed to the effect of airborne chlorides carried by the sea wind.

2.3 Tests

The evaluation of chloride penetration was based on the assessment of the chloride content of the samples taken at various depths at successive time intervals. Samples with 5 mm depth increments were obtained for each time interval in two adjacent holes, drilled with a 20 mm bit. Once taken, the samples were analysed to determine their total chloride content, using a chloride ion selective electrode. The results were expressed as a percentage of chlorides, in relation to the mass of the concrete.

Carbonation depth was measured by the phenolphthalein test, in 90 mm diameter drill cores extracted from the test slabs, in accordance with the RILEM – CPC 18 recommendations [10].

Carbonation and chloride penetration were also measured periodically over a six-year period, in the case of the test slabs exposed in conditions A and B, and over a three-year period, in the case of the test slabs in condition C.

3. TEST RESULTS AND DISCUSSION

3.1 Carbonation of the concrete

Fig. 1 shows the average carbonation depths, measured in concrete slabs C1 and C2, throughout the exposure period.

The phenolphthalein test shows no signs of carbonation in concrete C3, in any exposure condition. The behaviour of this type of concrete must be associated with two types of factors: the first relates to the high cement content, which gives rise to a great accumulation of alkaline compounds; the second factor relates to the low water-cement ratio and to the incorporation of microsilica in the mix, which results in a closed pore structure with a very high resistance to carbon dioxide penetration.

Ho and Lewis [11] showed the importance of cement content and other studies [12-15] have shown the significance of water-cement ratio on the carbonation rate.

The research on the effect of microsilica has not produced consistent results. Nevertheless, Gjrv [16], in a study that summarises the conclusions of various experimental works, states that the test results show that the carbonation rate is significantly reduced in cases in which microsilica is used in combination with a superplasticiser.

The behaviour of concrete C3 was confirmed in short-term tests. No carbonation was detected by the phenolph-

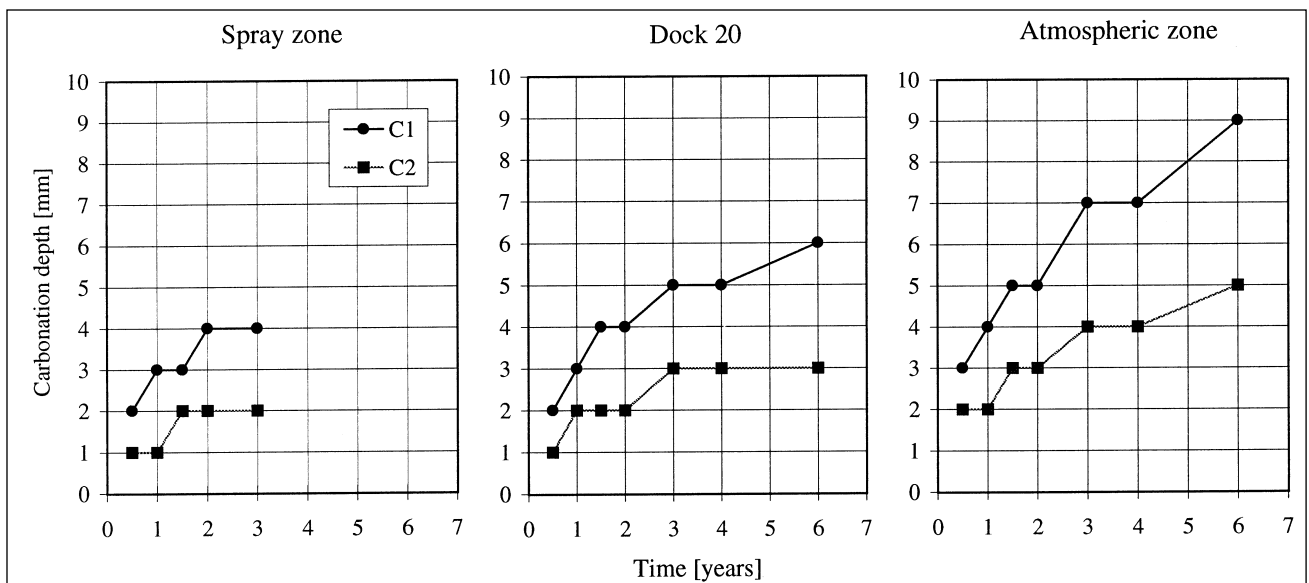


Fig. 1 – Mean carbonation depth on concrete samples C1 and C2.

thalein test, after one year of exposure in a carbonation chamber containing 5% of CO₂ and a relative humidity of 60% [8].

When the results for mixes C1 and C2 are compared, it is found that the carbonation rate of concrete C2 is much lower in all exposure conditions. The W/C and the cement content are the main causes of the different behaviour of these two types of concrete.

Fig. 1 shows that exposure conditions also have a major effect on the carbonation rate. The highest carbonation rates occurred in the atmospheric zone (C), while the lowest rates occurred in the spray zone (A). The behaviour of the mixes in the various exposure conditions is associated with the concrete moisture content. In the atmospheric zone, the test slabs are subject to lower humidity conditions than those within the dock and in the spray zone; as in the latter circumstances, the test slabs are subject to cycles of wetting by the estuary waters, in addition to rainwater.

A decline of the carbonation rate over exposure time was noted in most cases. This aspect is related to the reduction of the concrete porosity due to the formation of calcium carbonate as a consequence of carbonation reactions. Other factors that can determine this behaviour are the humidity content within the concrete and the hydration of the cement throughout the exposure period.

In a structure exposed to wetting and drying cycles, the relative humidity within the concrete tends, on average, to be greater than the relative humidity of the environment, as the concrete absorbs water more rapidly than it loses it [17, 18]. The degree of saturation of the concrete pores will therefore, on average, be greater in the inner layers, which limits CO₂ penetration, and gives rise to a reduction in the carbonation rate.

Cement hydration throughout the exposure period leads to a reduction of the concrete porosity and accordingly, to a reduction in the carbonation rate.

3.2 Long-term prediction of concrete carbonation

Carbon dioxide penetrates into concrete by a diffusion process, with a concentration gradient of CO₂ acting as the driving force. This mechanism can be modelled by a formula based on Fick's diffusion law which describes the relation between carbonation and time [18, 19]:

$$x = K \sqrt{t}$$

where x is the carbonation depth after time t and K is the carbonation coefficient.

In the derivation of this formula the diffusion coefficient for carbon dioxide in concrete has been taken as a constant. However, the diffusion coefficient is not independent of time and depth and varies strongly with the moisture content in the concrete pores as discussed by Kropp [19]. So, from a theoretical point of view the application of Fick's law of diffusion has some limitations.

Nevertheless, the above equation is a good approximation for the carbonation depth variation with time and is found valuable for carbonation in concrete by many authors [11, 20-22]. A very simple formula is proposed to model concrete carbonation:

$$x = a + K_1 \sqrt{t} \quad (1)$$

where a is the initial depth of carbonation after the curing period.

In this equation, carbonation depth evolution is considered to be proportional to \sqrt{t} . It is however found that the carbonation rate in structures exposed to the exterior environment tends to be less than that given by this ratio [19, 23], and the following alternative formula is proposed:

$$x = K_2 t^n \quad (2)$$

Hilsdorf [23] states that the parameter n is generally less than 0.5, and lies in the $0.2 < n < 0.5$ interval.

Parameters a , K_1 , K_2 and n were determined for each type of concrete and exposure condition, by a regression analysis of Equations (1) and (2) regarding the experimental results. Table 4 shows the values of K_1 , K_2 and n .

Concrete type	Exposure condition	K_1 [mm/year ^{0.5}]	K_2 [mm/year ^{n]}	n
C1	A	2.00	2.75	0.40
	B	2.17	2.95	0.43
	C	3.38	4.03	0.44
C2	A	1.18	1.31	0.48
	B	1.14	1.62	0.43
	C	1.81	2.39	0.40

The values obtained for parameter a are very low, less than 0.8 mm, and can accordingly be neglected in the analysis of long-term carbonation.

The analysis of the values obtained shows that the carbonation depth evolution is, in all cases, less than that given by the \sqrt{t} ratio.

The value of n varies from 0.40 to 0.44 for concrete C1 and from 0.40 to 0.48 for concrete C2, there being no standard variation as a function of exposure conditions.

Parameter K_2 is significantly dependent on both the type of concrete and exposure conditions. The influence of the quality of the concrete is given by a ratio between the K_2 parameters, which varies from 2.1 to 1.7, for the spray zone and the atmospheric zone, respectively. There are also significant variations of this parameter, associated with the various exposure conditions for the same type of concrete, of an order of magnitude of approximately 1.5 and 1.8 for concrete C1 and C2 respectively.

The comparison of the behaviour of the concrete mixes is made easier if Equation (1) is considered as it incorporates only one parameter, K_1 . This parameter characterises the resistance to carbonation. Using this approach, it is found that concrete C2 is approximately 1.7 to 1.9 times more resistant to carbonation than concrete C1, depending on the exposure conditions. The rate of carbonation in C1 and C2 mixes is approximately 1.7 and 1.5 times, respectively, higher in the atmospheric zone than in the spray zone.

The long-term evolution of carbonation for the various exposure conditions and types of concrete can be

determined on the basis of K_2 and n parameters calculated, using Equation (2). This analysis makes it possible to determine the period of time necessary for the carbonation front to reach the reinforcement level. Fig. 2 presents the graphs that show the evolution of carbonation in the various cases analysed.

The results indicate that, for the concrete mixes studied, carbonation reaches small depths after long exposure periods (over 100 years) in any of the exposure conditions. The carbonation depth predicted for the poorer quality concrete (C1), subject to the most aggressive exposure condition, after 120 years of exposure, is only 33 mm. At the end of the same period, concrete C2 has a carbonation depth of approximately half the carbonation depth of concrete C1.

The graphs show that the difference between the performance of the two types of concrete increases with the carbonation rate. After 120 years of exposure in the atmospheric zone, concrete C1 shows a carbonation depth that is approximately two times greater than that of concrete C2, while in the spray area this ratio drops to 1.4 times, *i.e.* the increase of the moisture content of the concrete attenuates the behaviour difference in relation to carbonation. The prediction of carbonation depth evolution on the basis of Equation (1), neglecting the parameter a value, was also introduced into the graphs and it was found that in some cases the results varied from the data obtained by using Equation (2) as exposure time increased. These differences are, however, not very significant, even after an exposure period of 120 years. It must nevertheless be borne in mind that it is unrealistic to make strict comparisons between these equations, as the equations were obtained from a limited number of results. No major errors will, in principle, be made if Equation (1) is applied to the long-term prediction of carbonation evolution.

3.3 Chloride penetration

In this experimental study, chloride penetration was measured at successive time intervals during the exposure period. A model was developed to evaluate the long term chloride penetration, based on the experimental results, taking the time dependence of the chloride diffusion coefficient and surface chloride content into consideration [24, 25].

The penetration depth of the critical chloride content x_{cr} after the time t is given by the following equation:

$$x_{cr} = 2 \sqrt{D_1 t^{1-m}} \cdot \operatorname{erf}^{-1} \left(1 - \frac{C_{cr}}{C_1 t^n} \right) \quad (3)$$

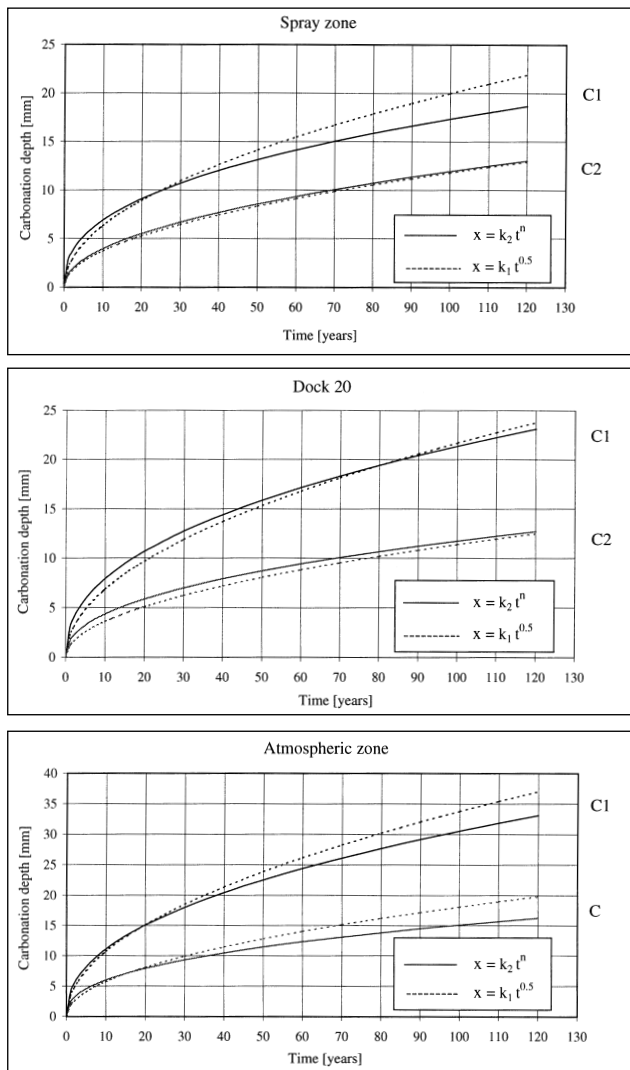


Fig. 2 – Long-term prediction of concrete carbonation.

where D_1 and C_1 are the chloride diffusion coefficient and the surface chloride content respectively, after one year of exposure; n and m are empirical coefficients and C_{cr} is the critical chloride content.

The values of the above mentioned parameters, determined on the basis of the experimental results, are indicated in Table 5.

Table 5 – Values of the diffusion coefficient D_1 , surface chloride content C_1 and coefficients m and n for concrete types C1, C2 and C3

Concrete type	Exposure condition	D_1 [mm ² /year]	m	C_1 [% wt. of concrete]	n
C1	A	98.7	0.51	0.24	0.47
	B	95.9	0.44	0.21	0.47
	C	38.2	0.42	0.12	0.54
C2	A	50.5	0.43	0.20	0.51
	B	41.3	0.41	0.14	0.54
	C	24.3	0.36	0.09	0.69
C3	A	43.7	0.45	0.22	0.48
	B	28.5	0.38	0.12	0.59
	C	21.2	0.40	0.10	0.59

3.4 Comparison between carbonation and chloride penetration

The evolution of carbonation and penetration of the critical chloride content, in the types of concrete considered and in the different exposure conditions, given by Equations (2) and (3), is represented in Fig. 3.

For the critical chloride content a value of 0.4% of the mass of cement was taken into consideration. This value, measured in relation to the mass of concrete, corresponds to 0.05%, 0.07% and 0.08% for concrete mixes C1, C2 and C3 respectively.

The graphs show that chloride penetration is much more significant than concrete carbonation in all exposure conditions. For example, it is predicted, in the case of dock 20 (B), that the carbonation depth will, after 60 years, be 17 mm and 9 mm respectively for concrete C1 and concrete C2, while critical chloride content penetration reaches depths of 82 mm and 53 mm respectively.

In the atmospheric zone, the difference between the carbonation rate and the chloride penetration rate is attenuated, although it is still significant. This behaviour is fundamentally due to two types of factors: the first relates to the moisture content of the concrete, which has its origin in the exposure environment; the second factor relates to the level of chloride contamination in the exposure environment.

In the atmospheric zone, the moisture content of the concrete is lower than in other exposure conditions,

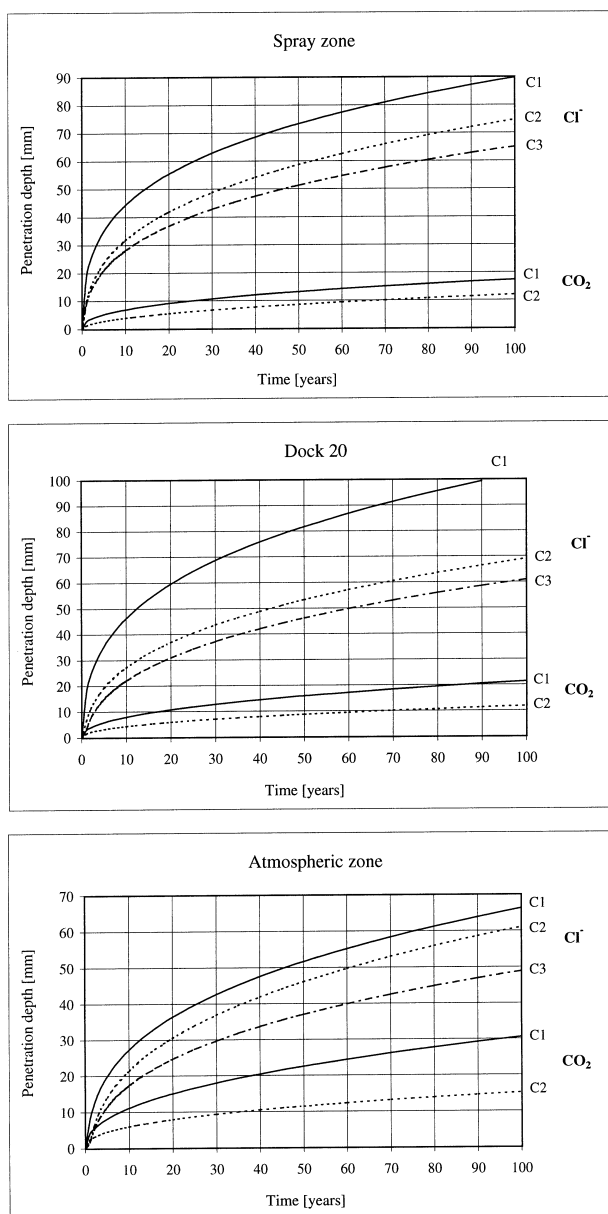


Fig. 3. – Long-term prediction of chloride and carbonation penetration.

which gives rise to higher carbonation rates and to lower chloride penetration rates. For chlorides, penetration only occurs in pores that contain water, unlike carbonation. In the atmospheric zone, on the other hand, the concrete is not in direct contact with sea water. Because the penetration by absorption is absent and the chloride content at the surface of the concrete is much lower than in the other exposure conditions, the penetration of chlorides by the diffusion mechanism is reduced.

In the marine environment, high quality concrete and an optimum concrete cover thickness should be used in order to ensure that structures have adequate durability. In these conditions, the carbonation mechanism is of little significance, as can be seen from the behaviour of concrete mixes C2 and C3. In the atmospheric zone, the

carbonation depth predicted for concrete C2 after 60 years is only 12 mm. This figure accounts for only a small part of the concrete cover layer, which should be used given the effect of chlorides, as shown in Fig. 3.

However, in structures made of poor quality concrete exposed to the marine atmospheric zone, the rate of carbonation can be very high, namely in dry climates. In this situation the carbonation depth can exceed the chloride penetration depth. The combined effect of carbonation and chlorides leads to an early depassivation of steel and to high corrosion rates, causing severe damage on the structures.

4. CONCLUSIONS

In the marine environment, exposure conditions and concrete quality have a major influence on the concrete carbonation rate. The highest carbonation rates occur in the atmospheric zone, where the moisture content of the concrete is lowest. Unlike carbonation, the lowest chloride penetration rates occur in the atmospheric zone.

In structures constructed with poor quality concrete and exposed to the marine atmospheric zone, chloride penetration and carbonation can play a significant role in the deterioration process, as was shown in an inspection of 25-year-old concrete structures in a dockyard.

However, the experimental results obtained in this study and the long-term predictions for chloride penetration and carbonation show that the carbonation rate in medium and high quality concrete is much less than the chloride penetration rate in any exposure zone of the marine environment.

The need to use high quality concrete and optimum reinforcement cover to protect structures from the effect of chlorides, indicates that the carbonation mechanism is of little significance in a marine environment and is not, therefore, a source of concern.

REFERENCES

- [1] Appleton, J. and Costa, A., 'Deterioration and repair of the Setenave concrete dockyards', *Portuguese Review of Structural Engineering*, **37** (1994) 43-50.
- [2] Costa, A. and Appleton, J., 'Inspection and repair of 4 wharves', in: Portuguese Conference on Structural Engineering 98 (LNEC, Lisbon, 1998) 373-382.
- [3] Kayyali, O. A. and Haque, M. N., 'Effect of carbonation on the chloride concentration in pore solution of mortars with and without fly ash', *Cem. Concr. Res.*, **18** (4) (1988) 636-648.
- [4] Roper, H. and Baweja, D., 'Carbonation-chloride interactions and their influence on corrosion rates of steel in concrete', in: Malhotra, V. (ed), 'Durability of Concrete' ACI SP-126 (American Concrete Institute, Detroit, 1991) 295-315.
- [5] Tumidjaski, P. J. and Chan, G. W., 'Effect of sulphate and carbon dioxide on chloride diffusivity', *Cem. Concr. Res.*, **26** (4) (1996) 551-556.
- [6] Suryavanshi, A. K. and Swamy, R. N., 'Stability of Friedel's salt in carbonated concrete structural elements', *Cem. Concr. Res.*, **26** (5) (1996) 729-741.
- [7] Al-Khaiat, H. and Haque, M. N., 'Carbonation of some coastal structures in Kuwait', *ACI Mater. J.*, **94** (6) (1997) 602-607.
- [8] Costa, A., 'Durability of concrete structures in marine environment', Doctoral Thesis, Instituto Superior Tecnico Lisbon (1997).
- [9] ISO/DP 9225, 'Corrosion of Metals and Alloys. Corrosivity of atmospheres. Methods of measurements of pollution', (1989).
- [10] RILEM Recommendation CPC-18, 'Measurement of hardened concrete carbonation depth', *Mater. Struct.*, **17** (1984).
- [11] Ho, D. W. S. and Lewis, R. K., 'Carbonation of concrete and its prediction', *Cem. Concr. Res.*, **17** (3) (1987) 489-504.
- [12] Ho, D. W. S. and Lewis, R. K., 'The specification of concrete for reinforcement protection - performance criteria and compliance by strength', *Cem. Concr. Res.*, **18** (4) (1988) 584-594.
- [13] Parrot, L. J., 'Carbonation, corrosion and standardization', in: Dhir, R., Green, J. (eds), 'Protection of Concrete' (E&FN Spon, 1990) 1009-1023.
- [14] Tuutti, K., 'Corrosion of steel in concrete' (Swedish Cement and Concrete Research Institute, Stockholm, 1982).
- [15] Uomoto, T. and Takada, Y., 'Factors affecting concrete carbonation rate', in: Nagataky, S., Nireki, T., Tomosaka, F. (eds), 'Durability of Building Materials and Components' (E&FN Spon, 1993) 1133-1141.
- [16] Gjørø, O. E., 'Effect of condensed silica fume on steel corrosion in concrete', *ACI Mater. J.*, **92** (6) (1995) 591-598.
- [17] Schiessl, P., 'Transport mechanisms in concrete', in: Bulletin d'Information n° 183 CEB (ed), 'Durable Concrete Structures' (Comité Euro-International du Béton, 1993).
- [18] Bakker, R., 'Initiation period', in: Schiessl, P. (ed), 'Corrosion of Steel in Concrete' (RILEM Report, Chapman and Hall, 1988) 22-55.
- [19] Kropp, J., 'Relations between transport characteristics and durability', in: Kropp, J., Hilsdorf, H. (eds), 'Performance Criteria for Concrete Durability' (RILEM Report 12, E&FN Spon, 1995) 97-137.

- [20] Broomfield, J. P., 'Corrosion of steel in concrete. Understanding, investigation and repair', (E&FN Spon, 1997).
- [21] Potter, R. and Ho, D., 'Quality of cover concrete and its influence on durability', in: Scanlon, J. (ed), 'Concrete Durability' ACI SP-100 (American Concrete Institute, Detroit, 1987) 423-445.
- [22] Schubert, P., 'Carbonation behavior of mortars and concretes made with fly ash', in: Scanlon, J. (ed), 'Concrete Durability' ACI SP-100 (American Concrete Institute, Detroit, 1987) 1945-1962.
- [23] Hilsdorf, H. K., 'Concrete', in: Eibl, J. (ed), 'Concrete Structures Euro-Design Handbook 1994/96' (Ernst & Sohn, 1994) 1-103.
- [24] Costa, A. and Appleton, J., 'Chloride penetration in marine environment - Part I: Main parameters affecting chloride penetration', *Mater. Struct.* **32** (1999) 252-259.
- [25] Costa, A. and Appleton, J., 'Chloride penetration in marine environment - Part II: Prediction of long term chloride penetration', *Mater. Struct.* **32** (1999) 354-359.