# Chloride profiles and diffusion coefficients in structures located in marine environments

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Steel corrosion is one of the main causes of damage in reinforced concrete structures. Recent studies carried out in Argentina indicate that the percentage of damage in concrete structures induced by corrosion of reinforcement is 16%. In structures located in marine environments the corrosion is due fundamentally to the action of chlorides. Chlorides penetrate concrete by different processes; in structures exposed to atmosphere, the ingress process is by diffusion. Ingress depends on the characteristics of concrete and of its distance to the sea (marine environment). In this paper, assessment of durability of concrete structures exposed to marine (Atlantic Ocean coast) environments is reported. The ages of the evaluated structures, bridges and buildings, vary between five and 67 years. Surface chlorides concentration (environmental loads) and the effective diffusion coefficient, calculated using Fick's second law, are included. Furthermore, the quality of the cover concrete is characterised by means of the specific gravity and porosity accessible to water methods.

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## Introduction

Steel corrosion is one of the main causes of damage in reinforced concrete structures.[1] Recent studies carried out in Argentina indicate that the percentage of damage in concrete structures induced by corrosion of reinforcement is 16%.[2]

In marine environments, corrosion of reinforcement in concrete structures is induced by the presence of chloride ions. The location and type of structural elements can induce chloride ingress due to capillary absorption, permeability or diffusion processes. In some cases, the ingress mechanisms can be multiple, for example, in bridge pillars. In those structures in contact with marine atmospheres, chlorides migrate through concrete by diffusion processes.[3,4]

The chloride diffusion process takes place if there is a difference of concentration between the environment and concrete and this process is of great significance because the majority of the structures are in contact with the atmosphere. Furthermore, it depends on the distance and location of the structure from the original source of the chloride. Other variables are the quality of the cover concrete composition (water/cement ratio, cement type, use of mineral additives), density and type and time of the concrete curing. These variables affect the pore size distribution and porosity of the concrete, and therefore they produce the conditions for the diffusion process.

Chlorides can also be introduced at the time of construction, principally with admixtures, water and/or fine or coarse aggregates. The chloride ions, present in the mix, react in different ways: part of them forms insoluble salts, another part forms soluble salts (salt of Friedel) and a third part can be found in the concrete as free chlorides.

The chloride ions that participate in the corrosion of reinforced concrete structures are the free chlorides (chloride in the pore water) and part of the soluble chlorides.[5]

In old structures with carbonated concrete, the bond chlorides are liberated and consequently the risk of reinforcement corrosion may be increased.

In the present study different types of concrete structures exposed to marine environments were evaluated. In all cases the reinforcement corrosion of structures must be attributed to the presence of chlorides. The effective chloride diffusion coefficients and the surface chloride concentration have been evaluated and the influence of the height in buildings and the roughness of the surface at the ingress of chlorides were also analysed. In addition, the quality of the cover concrete was analysed by means of the specific gravity and porosity methods.

## Diffusion process in concrete

The chloride concentration in concrete, at a certain age and distance from the surface, can be evaluated by using Ficks's second law. For one-dimensional chloride diffusion, the solution takes the following form[6]

$$C(x,t) = C_0 + (C_s - C_0)\, erf_c[x/2(D_{cl,eff}\, t^{0\cdot5}]$$

where $C(x,t)$ is the chloride content at depth $x$ and time $t$; $C_s$ is the surface chloride concentration (environmental load); $C_0$ is the initial chloride content incorporated with concrete component materials; $x$ is the depth from exposure surface; $D_{cl,eff}$ is the effective diffusion coefficient; $t$ is the exposure time (age of the structure); and $erf_c$ is the error function complement.

The effective diffusion coefficient depends, among other factors, on the exposure time. In particular, it can be said that $D_{cl,eff}$ decreases in time due to the cement hydration processes that modify the pore system. This modification is greater when active mineral additions are employed, such as silica fume, fly ash, etc. Furthermore, the roughness of the surface and rainfall both modify the $C_s$ value. This fact influences the chloride ingress because the environmental load is modified.

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**Figure 1 Building 1—showing spalling and loss in steel section**

△ **Figure 2 Building 3—showing that the bars are no longer in contact with the concrete**

Nevertheless, when some concrete structure pathologies exist, for example cracking caused by alkali–silica reaction, the diffusion coefficient can increase, as new ways of chloride ingress (cracks) exist in addition to those of the initial pore system, due to the atmosphere.[7]

Moreover in concrete that is exposed to the atmosphere, the superficial zone (approximately 5 mm) is affected by rain, which reduces the chloride content. This situation is not considered in the Fick's second law solution.

## Evaluated structures

Several bridges and buildings located in different zones of the Province of Buenos Aires, Argentina, near to the Atlantic Ocean coast, that are exposed to airborne salt but not in direct contact with sea water (class designation XS1 according to European Standard—CEN,1999) were evaluated.[6] In all the evaluated structures corrosion damage was observed (see Figures 1 and 2).

Bridge 1 (aged 67 years) and bridge 2 (aged 51 years) are located on the same water stream, at distances of 250 and 100 m, respectively, from the sea. Bridge 3 (aged 65 years) is located on another water stream and at a distance of approximately 1500 m from the sea. In these cases, winds blow off the sea towards the coast and no significant obstacles exist between the sea and the bridges.

The other structures evaluated were buildings 1 and 2, with ages of 5 and 30 years, respectively, which are located on the same street, perpendicular to the shoreline and at distances of 200 and 600 m, respectively. The other example is building 3, which is 15 years old and located at a distance of 150 m from the shore line with no obstacle between it and the sea.

In all the evaluated structures, the concrete mix included quartzitic crushed stone as coarse aggregate, sea sand containing about 15% shell fragments as fine aggregate and normal Portland cement (Type I ASTM) of the same origin.

The evaluated structures, the different pathologies observed (colour changes, cracking, spalling, loss of steel section and deflection of beam) are shown in Table 1 and the damage levels are qualified according to the mentioned specification.[8] In the cases of structures identified as having damage levels C and D, it will be necessary to carry out urgent repairs to the structure in order to extend its service life.

## Characteristics of cover concretes

Samples of the cover concretes were extracted from the evaluated structures. Specific gravity saturated and surface dry ($SG_{ssd}$) and porosity

**Table 1 Damage levels determined in the evaluated reinforced concrete structures**

| Visual indication | Structures | | | | | |
|---|---|---|---|---|---|---|
| | Bridge 1 | Bridge 2 | Bridge 3 | Building 1 | Building 2 | Building 3 |
| Colour changes | Rust stains | Rust stains | Rust stains | — | — | — |
| Cracking | Extensive | Several | Several | Extensive | Several | Extensive |
| Spalling | Extensive | Some | Some | Extensive | Some | Extensive* |
| Loss in steel section | 10% | 5% | 5% | 25% | ~5% | ~30% |
| Deflection | — | — | — | — | — | Apparent† |
| Damage levels | C | B | B | D | B | D |

* In some zones, bars are no longer in contact with concrete. This situation is observed in ground-floor columns.
† Deflection is detected in some structural elements, particularly beams.

**Table 2 Characteristics of the cover concrete**

| Structures | Age: years | Distance from sea: m | $SG_{ssd}$ | $P$: % | $C_s$: kg/m$^3$ | $D_{cl,eff}$ $10^{-12}$: m$^2$/s |
|---|---|---|---|---|---|---|
| Bridge 1 | 67 | 250 | 2·24 | 18·4 | 4·1 | 1·37 |
| Bridge 2 | 51 | 100 | 2·38 | 13·5 | 4·6 | 0·02 |
| Bridge 3 | 65 | 1500 | 2·43 | 11·9 | 2·6 | 0·04 |
| Building 1 | 5 | 200 | 2·18 | 13·2 | 2·4 | 0·97 |
| Building 2 | 30 | 600 | 2·34 | 12·8 | 1·2 | — |
| Building 3 | 15 | 150 | 2·28 | 7·8 | See Table 3 | 1·20 |

($P$), accessible to water, were determined. Porosity was calculated as the ratio of the total volume of the pores accessible to water to the volume of the sample.[9] Chloride content on the exposed concrete surface ($C_s$) and the effective diffusion coefficient ($D_{Cl,eff}$) were calculated by means of an analysis of non-linear regression considering the chloride profile. For this purpose, four small slices, 5 mm thick, were cut by means of a diamond disc in the dry state. The material was crushed and the free and soluble chlorides were determined by chemical analysis after the concrete had been allowed to stand for 24 h in water.

To calculate the effective diffusion coefficients, the value of $C_0$ (initial chloride concentration) is considered null, despite the use of sea sand as fine aggregate. This value was adopted because the chloride content in sands in the area in which the structures are located indicates percentages of about 0·01% (in weight).

The values of $D_{Cl,eff}$ and $C_s$ may not necessarily represent chloride diffusion coefficient and surface chloride concentration; instead they may simply represent the regression coefficients obtained from curve fitting of the chloride profiles and can be used to compare concretes of different qualities. This last scenario is valid for laboratory studies and assessment of concrete structures affected by corrosion.

The characteristics of cover concrete are presented in Table 2. The values shown correspond to the average of a minimum of three determinations.

In building 2, $C_s$ and $D_{cl,eff}$ were not determined because the chloride profile was practically constant throughout the thickness of the cover concrete (25 mm).

In building 3, the surface chloride concentration was determined at two different heights of the building, for two concrete surfaces: facing the sea; and back to the sea, namely the surface protected from the marine winds (see Table 3).

It has generally been assumed that theoretically the surface chloride concentration depends, among other variables, on the roughness of the concrete surface. For this reason laboratory experiments were performed with concretes of different porosity, mixed with the same materials. In Table 4, the values of $C_s$ determined on both smooth and rough concrete surfaces are presented. The evaluations were carried out at an age of 120 days using samples submerged in a solution of 3% sodium chloride. The reported values correspond to the average of a minimum of five determinations.

## Analysis of results

The surface chloride concentration values determined for bridges 2 and 3, in sectors of similar characteristics (beams of the board) and with similar ages and porosity, demonstrate the influence of the distance from the sea. A similar behaviour is observed in the results obtained for the buildings.

Results obtained for building 3 indicate that the height and the exposed face to the sea have a significant influence on the surface chloride concentration. The greatest damage due to corrosion was detected in the surfaces

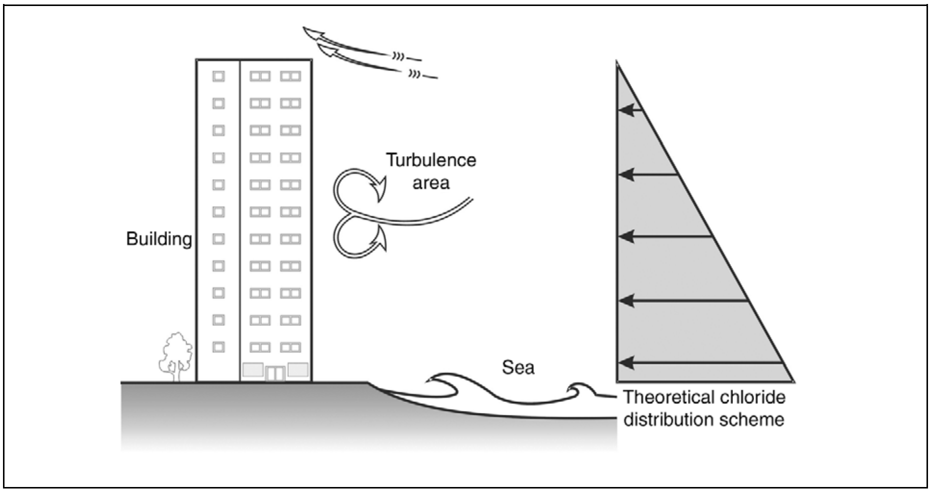
**Table 3 Surface chlorides concentration in concrete of building 3**

| Height above floor: m | Surface chlorides concentration: kg/m$^3$ | |
|---|---|---|
| | Facing the sea | Back of building |
| 5·0 | 4·9 | 1·3 |
| 10·0 | 0·3 | — |

**Table 4 Surface chlorides concentration in concretes with different types of surface**

| Concrete | Porosity: % | Surface chloride concentration: kg/m$^3$ | |
|---|---|---|---|
| | | Smooth surface* | Rough surface† |
| 1 | 11·4 | 6·3 | 7·3 |
| 2 | 13·8 | 8·9 | 9·2 |

* Specimen's face in contact with metallic moulds.
† Fracture surface obtained in beam flexion tests.




△ **Figure 3 A possible theoretical distribution of the surface chloride concentration on the building surface that faces the sea**

facing the sea and in the lower sectors of the structures, particularly in ground-floor columns. This statement is valid only in those regions where the wind blows from the sea.

When no obstacles exist between the sea and the structure, greater deposits of chlorides were determined in the lower part of the building. In Figure 3 a scheme of a possible theoretical chloride distribution is presented, which is similar to the distribution of dust being carried and settled by the wind on the structure surface.[10] The structural design and the rainfall pattern can eliminate the layers of deposits and cyclically modify the surface chloride concentration.

Test results indicate that the effective diffusion coefficient depends on the porosity of the concrete. This situation can be observed in bridges 1 and 2, in which the surface chloride concentration is similar but the concrete porosity varies widely, and so, effective diffusion coefficients have different values for similar ages.

In the cover concretes of building 2, constant values of chlorides were determined. This indicates that diffusion processes due to chlorides from the atmosphere were not being detected. The chloride content of the concrete must be ascribed to the use of calcium chloride as an accelerator, added to the mixture, which was a regular practice in Argentina during the time when the structure was built.

## Final considerations

All the evaluated structures located in marine environments presented evidence of corrosion damage of different magnitude. The influence of cover concrete quality on the penetration of chlorides by diffusion processes was confirmed. In particular, concrete porosity seems to be the main variable in the diffusion process.

Surface chloride concentration, that represents the environmental load, depends directly on the distance from and alignment of the surface with respect to the sea. This parameter also varies with the height of the building.

For structures located in aggressive atmospheres due to the presence of chlorides, calculation of the cover concrete thickness taking account of the diffusion coefficient obtained in laboratory experiences with samples in aqueous solution yields values of required thickness that are larger than necessary, because the diffusion coefficient decreases with the time of exposure. For this reason the use of real values of the effective diffusion coefficient determined in old concrete structures, apparently provokes a substantial decrease in values of the cover concrete depth required. Consequently the building economic cost would be lower while maintaining a similar service life.

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