

## 5. CONCRETE SERVICE LIFE REGARDING CARBONATION

### 5.1 Physicochemical considerations

The majority of concrete deterioration cases is connected to corrosion of reinforcement due to *carbonation- or chloride-induced depassivation of steel bars* [1,3,10]. In concrete, reinforcing bars are protected from corrosion by a thin oxide layer which is formed and maintained on their surface due to the *highly alkaline environment* of the surrounding concrete (pH values around 12.6). The alkalinity of the concrete mass is due to the  $\text{Ca}(\text{OH})_2$  produced during the reaction of the cement with water; cement hydration, see 3.1.1. Depassivation of the reinforcing bars occurs either when chloride ions diffuse in the pore water and reach the bars or when the pH value of the concrete surrounding the bars drops below 9, due to diffusion of atmospheric  $\text{CO}_2$  and its reaction with the  $\text{Ca}(\text{OH})_2$  of the concrete mass, or by a combination of these two mechanisms, in which the second mechanism accelerates the first, Fig. 5.1.1.

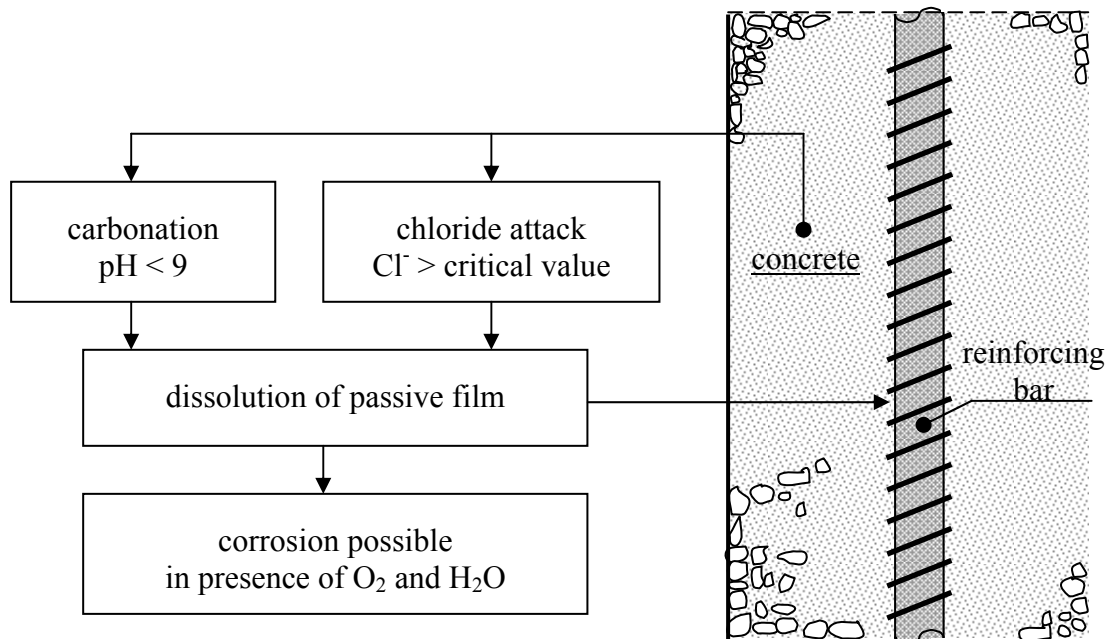


Figure 5.1.1 Initiation mechanisms of corrosion in concrete.

The former mechanism (chloride penetration) predominates in marine environments, in coastal areas, and when deicing salts come in contact with the concrete surface (pavements and bridge decks, floors of parking garages, etc.). In urban and industrial areas, where environmental pollution results in a significant concentration of carbon dioxide, *carbonation-initiated reinforcement corrosion* prevails [7,74-76].

The carbonation of concrete is a complex physicochemical process. The process takes place in the cementitious components of concrete, whereas aggregates, which constitute the major part of the mass and volume of concrete are essentially an inert filler, at least as far as carbonation is concerned. However, since the presence of aggregates affects certain important parameters, such as the effective diffusivity of  $\text{CO}_2$ , all quantities used in the model refer to the total mass of concrete.

The process of carbonation involves *gaseous, aqueous and solid reactants* (Fig. 5.1.2). The solids which react with  $\text{CO}_2$  include not only  $\text{Ca}(\text{OH})_2$ , but also the main strength component of cement paste CSH, and the unhydrated constituents of  $\text{C}_3\text{S}$  and  $\text{C}_2\text{S}$  [7,76,77]. *Water* is always present in larger or lesser amounts in the pores of the hardened cement paste and plays a key role in the process of carbonation. The role of water is twofold: first it blocks the pores and thus hinders diffusion of  $\text{CO}_2$  through the pores; second, it provides a medium for reaction between  $\text{CO}_2$  and  $\text{Ca}(\text{OH})_2$ .

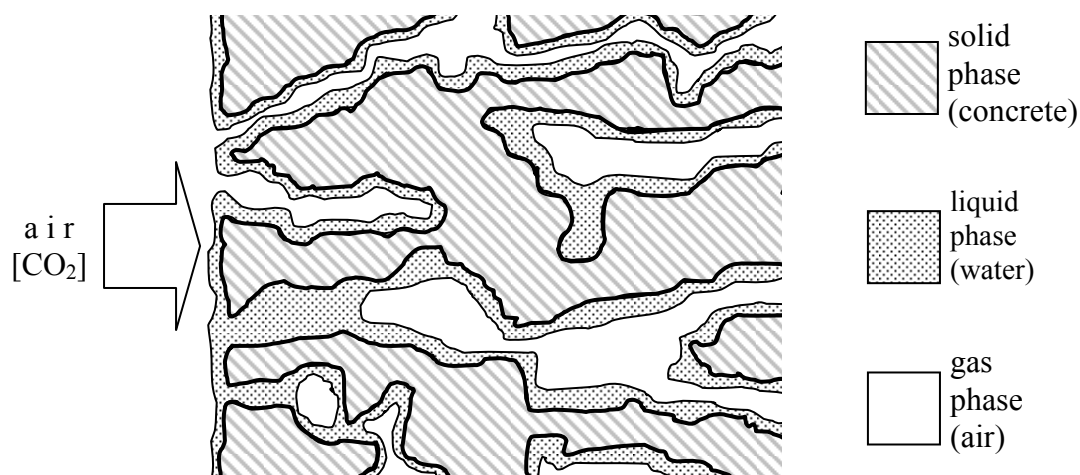
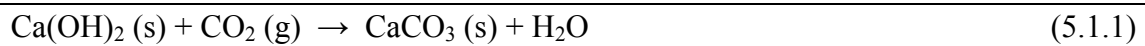


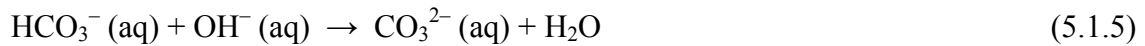
Figure 5.1.2 Schematic representation of concrete carbonation.

The above qualitative considerations can explain why the rate of carbonation has been reported to *go through a maximum with increasing ambient relative humidity* [1,7,74-78]. At very low ambient relative humidity levels, CO<sub>2</sub> can diffuse fast, but most pores are dry and the rate of carbonation is very slow. At high ambient relative humidity levels, practically all the pores are filled with water, therefore diffusion of CO<sub>2</sub> becomes very slow.

The *overall reaction* between solid Ca(OH)<sub>2</sub> (s) and diffused gaseous CO<sub>2</sub> (g),



consists of *several elementary steps* which take place in the aqueous film (aq) of the pore wall (Fig. 5.1.2). One can distinguish the Ca(OH)<sub>2</sub> dissolution step and other elementary steps:



All the principal reactants and products of the hydration reactions of cementitious materials are susceptible to carbonation in the presence of moisture. The ultimate carbonation products are normally alumina gel, calcite, iron oxide gel, and silica gel. The main reactions are:



There is a strong evidence that for the other hydrated and unhydrated constituents, carbonation is limited to a surface zone with the bulk of the crystallites remaining unaffected [22]. Consequently, carbonation of these components needs not to be included in the model.

## 5.2 Theoretical model

### 5.2.1 Usual range of parameters

Papadakis et al. [77,78] were the first to develop a reaction engineering model of the processes leading to concrete carbonation. These processes include the diffusion of CO<sub>2</sub> in the gas-phase of pores, its dissolution in the aqueous film of these pores, the dissolution of solid Ca(OH)<sub>2</sub> in pore water, its ultimate reaction with the dissolved CO<sub>2</sub>, and the reaction of CO<sub>2</sub> with CSH. The mathematical model yields a nonlinear system of differential equations in space and time and must be solved numerically for the unknown concentrations of the materials involved.

For the usual range of parameters (especially, for ambient relative humidity  $RH \geq 55\%$ ), certain simplifying assumptions can be made, which lead to the formation of a *carbonation front*, separating completely carbonated regions from the ones in which carbonation has not yet started, see Fig. 5.2.1. For one-dimensional geometry and constant values of parameters, the evolution of the *carbonation depth*,  $x_c$  (m), with time,  $t$  (s), is given by the following analytical expression of Papadakis et al. [79-81]:

$$x_c = \sqrt{\frac{2D_{e,CO_2}(CO_2 / 100)t}{0.33CH + 0.214CSH}} \quad (5.2.1)$$

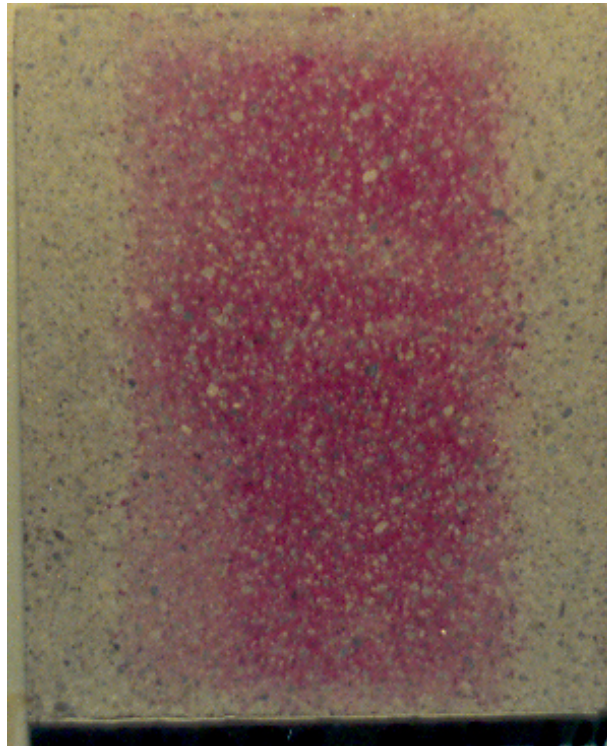
where, CO<sub>2</sub>: the CO<sub>2</sub>-content in the ambient air at the concrete surface (%), and D<sub>e,CO<sub>2</sub></sub>: the effective diffusivity of CO<sub>2</sub> in carbonated concrete (m<sup>2</sup>/s). CO<sub>2</sub>-content varies between 0.03%-0.15% (mean value for urban areas: 0.08%, whereas in countryside: 0.035%). In an ambient relative humidity, RH (%), the diffusivity is given by the empirical equation [31,81]:

$$D_{e,CO_2} = 6.1 \cdot 10^{-6} \left( \frac{\varepsilon_c - \varepsilon_{air}}{1 - \frac{A}{d_A} - \varepsilon_{air}} \right)^3 (1 - RH / 100)^{2.2} \quad (5.2.2)$$

The above equations are *valid for both portland and blended (with SCM) cements, as well when additions of type II are used separately in concrete [30,80-83]*. The **critical time,  $t_{cr,carb}$**  (s), required for the carbonation front to reach the reinforcement located at a distance  $c$  (concrete cover, m) from the outer surface, can be estimated by ( $RH \geq 55\%$ ):

$$t_{cr,carb} = \frac{(0.33CH + 0.214CSH)c^2}{2D_{e,CO_2}(CO_2/100)} \quad (5.2.3)$$

- ✚ **The service life of a concrete structure, regarding corrosion on reinforcement induced by carbonation, is at least  $t_{cr,carb}$ .**
- ✚ **As far as the steel bars have been depassivated, the corrosion progress depends on the relative availability of both water and oxygen.**



*Figure 5.2.1 Separation of carbonated (colourless) from a non-carbonated area (pink) in a typical concrete spraying by phenolphthalein solution.*

### 5.2.2 Very low relative humidity

Both thermogravimetric analysis and carbonation experiments have shown [78] that a sharp carbonation front is indeed formed for values of relative humidity above 50%. Under such conditions the evolution in time of the carbonation front is given by the simple analytical expression, Eq. (5.2.1). At lower RH values no sharp front is formed and the kinetics of the carbonation reactions become important. Comparison of the experimental results with the detailed reaction engineering model of Papadakis et al. [77] provides strong indication that the kinetics of the carbonation reactions are affected by the aqueous film thickness when the latter reaches molecular dimensions. When this is taken into account the model is in good agreement with experiment [78].

For **RH<55%**, the carbonation depth estimated by Eq. (5.2.1) has to be corrected multiplying it by the factor  $\lambda$  [78]:

$$\lambda = (RH/55)^2, \text{ i.e.,} \quad (5.2.4)$$

$$x_c = \lambda \sqrt{\frac{2D_{e,CO_2}(CO_2/100)t}{0.33CH + 0.214CSH}} \quad (5.2.5)$$

Similarly, for RH<55% the critical time  $t_{cr,carb}$ , required for the carbonation front to reach the reinforcement, Eq. (5.2.1), has to be corrected divided it by the factor  $\lambda^2$ , i.e.,

$$t_{cr,carb} = \frac{(0.33CH + 0.214CSH)c^2}{2D_{e,CO_2}(CO_2/100)\lambda^2} \quad (5.2.6)$$

In these unusual environmental conditions, concrete is protected against carbonation and in addition, the corrosion process is very slow due to the lack of the necessary water electrolyte; see next section 5.3.

### 5.3 Corrosion of the reinforcement in carbonated concrete

#### 5.3.1 Basic mechanisms

Corrosion reduces the available cross-sectional area of a reinforcing bar and hence its strength, and introducing a bursting internal pressure on the concrete surrounding the bar, since the volume of the corrosion products exceeds by far that of the corroding iron (Fig. 5.3.1). This causes *spalling of the concrete* covering the reinforcement and *splitting concrete cracks* parallel to the bar. Consequently, the connection between the reinforcement and the concrete is almost lost and the contribution of the former to the strength is drastically reduced.

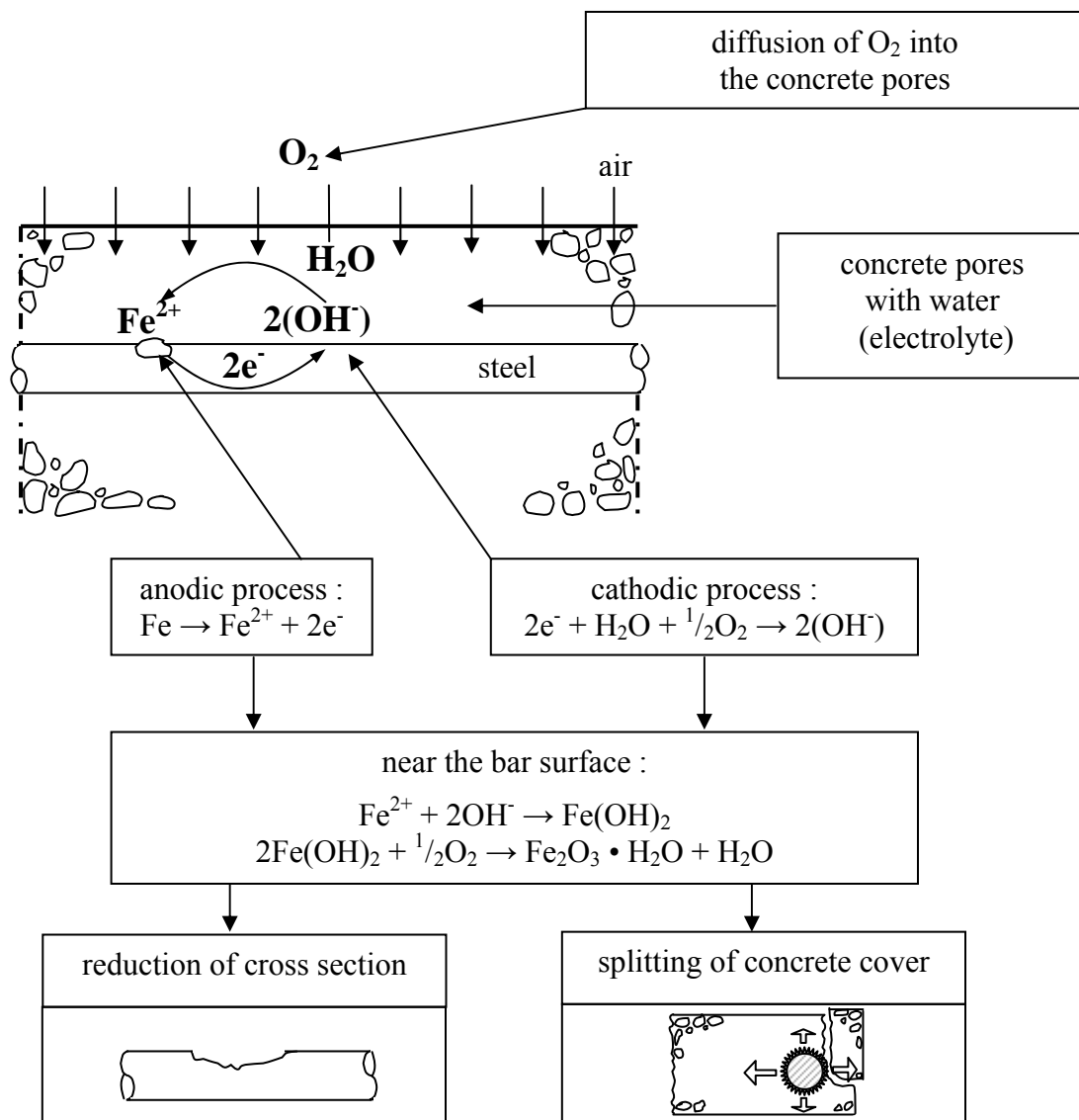
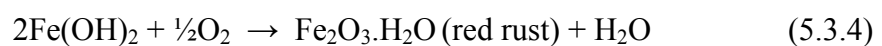


Figure 5.3.1 Mechanism and results of corrosion of steel in concrete.

Very often the safety and appearance problems caused by reinforcement corrosion before the end of the structure's useful lifetime are so severe that the structure either *has to be demolished* or *requires very costly general repair and strengthening*. In response to this serious problem, the engineering community has staged in recent years a significant research effort, aiming at developing a deeper understanding of the mechanisms leading to reinforcement corrosion as well as effective measures to control it.

In general, corrosion of metals can be divided into dry oxidation and wet corrosion. The *dry oxidation* is a very slow process that converts the pure metals, except gold and silver, to their more thermodynamically stable oxides. First, the metal forms an ion releasing electrons which convert oxygen to an ion. The ions attract each other to form an oxide. The rate of oxidation is controlled by the diffusion of species to the oxide layer. In the case of *wet corrosion*, the rate of metal loss becomes much more appreciable. As in dry oxidation, wet corrosion involves ionisation, but if ions are soluble in the corroding medium, usually water, the metal progressively corrodes. Areas of cathode and anode are distinguished in the metal surface, similar to an electrolytic cell, in which the following reactions take place, for the case of iron corrosion in water electrolyte, Fig. 5.3.1:



In a non-carbonated concrete the pore water (electrolyte) is in contact with the steel and due to its high pH the anodic product from Eq. (5.3.1) is not  $\text{Fe}^{2+}$  but is  $\text{Fe}_3\text{O}_4$ , which is deposited at the metal surface in a thin and dense form protecting from further corrosion (steel passivation). Due to loss of alkalinity by concrete carbonation this passivity is destroyed and corrosion takes place through Eq. (5.3.1)-(5.3.4). It has to be emphasized that oxygen and water must be always available at the cathode to ensure that the reaction (5.3.2) continues. Corrosion will occur neither in dry concrete (electrolytical process impeded) nor in water-saturated concrete (loss of oxygen), even if the passive layer at the surface of the reinforcement has been destroyed. The highest corrosion rate will occur in concrete surface layers, subjected to highly changing wetting and drying conditions.



### 5.3.2 Estimation of the corrosion propagation period

In reinforced concrete structures it can be reasonably assumed that major repair will be necessary once corrosion of the reinforcement causes *generalized cracking of the concrete cover*. Therefore such generalized cracking may be considered to signal the *end of the service life of the structure* ( $Z_{carb}$ ). The time to cracking the cover is equal to the period required for the carbonation front to reach the bar (*period to initiation of corrosion or corrosion incubation period*,  $t_{cr,carb}$ ) plus the time necessary for the layer of rust to build up around the bar to the thickness required to cause longitudinal splitting of the cover due to circumferential tension in concrete (*corrosion propagation period*,  $t_{pr,carb}$ ). According to Morinaga [84], on the basis of his extensive experimental program, under usual environmental conditions, the corrosion rate in carbonated concrete is so high that the arrival of the carbonation front at the bar is shortly followed by splitting of the concrete cover. Therefore the time  $t_{cr,carb}$  required for the carbonation front to penetrate the concrete cover  $c$  can be considered in good approximation as a narrow lower bound to the service life of reinforced concrete.

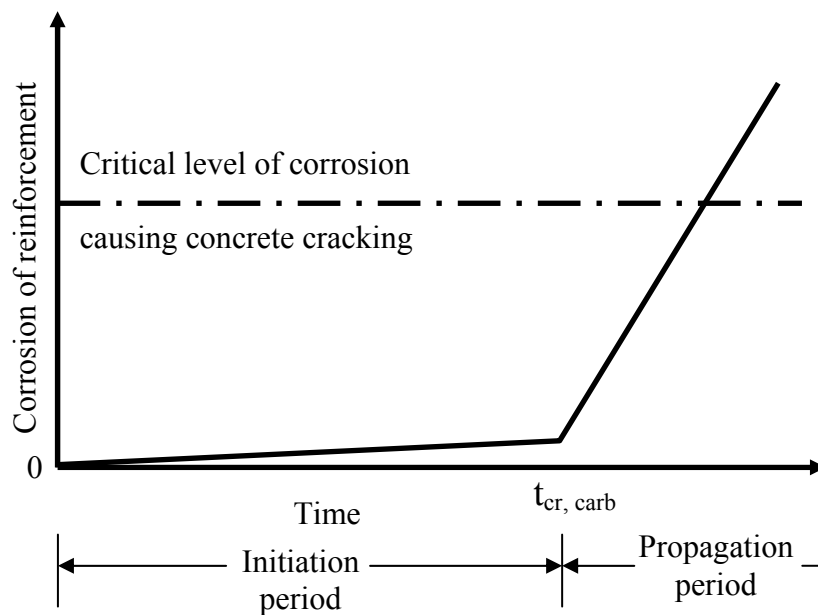


Figure 5.3.2 The two stages for corrosion damage in reinforced concrete.

If an approximation of the propagation period is required, then a full model of the physicochemical processes of corrosion and cracking has to be applied. However, until now there is no a generally accepted fundamental model for corrosion propagation of the concrete reinforcement [3,9,10,85]. This is due to complex phenomena of corrosion as well to the definition of detectable effects that define the limit of an acceptable damage, such as cracking degree. Further research is required to develop a reliable corrosion model with strong predictive capability.

An alternative approach in the interim would be to assume a propagation period of zero ensuring at least the lower limit for service life. However, this assumption is unfair, especially for low relative humidity when the propagation period is much higher than the initiation period due to lack of moisture. As a general conclusion from various works [10,84], the propagation period depends strongly on relative humidity. For RH in the region of 70% the propagation period is almost double of the initiation period, for RH in the region of 80% the propagation period is about the half of the initiation period, and for RH in the region of 90% the propagation period is about the 1/5 of the initiation period.

According to Morinaga [84,86], for usual environmental temperature (20 °C) and 55%<RH<95%, the rate of corrosion,  $q_c$  ( $10^{-4}$  g/cm<sup>2</sup>/yr), of the steel bar in concrete can be approached by the following empirical formula:

$$q_c = 65 (RH/100) - 35 \quad (5.3.5)$$

The critical amount of corrosion,  $Q_{cr}$  ( $10^{-4}$  g/cm<sup>2</sup>), that causes cracking and splitting of the cover  $c$  (mm), for usual concrete strength and 10mm diameter of reinforcing bar, can be approached by [84,86]:

$$Q_{cr} = 6 (1 + 0.2 c)^{0.85} \quad (5.3.6)$$

Thus, the propagation period (in years) can be approached by the ratio  $Q_{cr} / q_c$  :

$t_{pr,carb} = [6 (1 + 0.2 c)^{0.85}] / [65 (RH/100) - 35] \quad (5.3.7)$
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Finally, the service lifetime,  $Z_{\text{carb}}$  (in years), as regards the carbonation-induced corrosion of the concrete reinforcement, is the total sum of the two periods ( $t_{\text{cr,carb}}$  has to be converted in years dividing by 31,557,600s/yr):

$$Z_{\text{carb}} = t_{\text{cr,carb}} + t_{\text{pr,carb}} \quad (5.3.8)$$

### 5.3.3 Relationship with EN 206

As all concrete deterioration processes, carbonation and corrosion require water. However, corrosion is much faster than carbonation at higher water contents of concrete pores, and consequently at higher relative humidity of the ambient air [1,10,78]. This was taken into account in the definition of the exposure classes according to EN 206, and a correlation with the mean relative humidity of the ambient air is presented in Table 5.3.1 [this work; 1,10]. An estimation of the carbonation risk and the corrosion risk for various relative humidity regions is also presented [1].

We propose to use a measurable characteristic of the environment regarding its humidity state, i.e., *the mean relative humidity*, in order to convert the somehow indefinite exposure classes of EN 206. This *mean RH* could be the mean value within all the period under consideration.

Only reinforced concrete may deteriorate due to corrosion of reinforcement induced by concrete carbonation. For concrete without reinforcement or embedded metal there is no risk because changes caused to the concrete pores and constituents are not detrimental. For concrete with reinforcement or embedded metal and *exposure class X0* (very dry environment,  $\text{RH} < 45\%$ , mean value: 35%), due to insufficient moisture for the reactions, the carbonation rate is slight and there is no risk of corrosion.

**Table 5.3.1 Exposure classes according to EN 206 for possible corrosion induced by carbonation, correlation with measurable mean relative humidity RH and estimation of carbonation and corrosion risks.\***

Class	Description of the environment	Informative examples	RH (%)	Carb. risk	Corr. risk
<b>1 No risk of corrosion or attack</b>					
<b>X0</b>	For concrete with reinforcement or embedded metal: Very dry	Concrete inside buildings with very low air humidity	<45	1	0
<b>2 Corrosion induced by carbonation</b>					
Where concrete containing reinforcement or other embedded metal is exposed to air and moisture, the exposure shall be classified as follows:					
<b>XC1</b>	Dry	Concrete inside buildings with low air humidity	45-65	3	1
	Permanent wet	Concrete permanently submerged in water	>98	0	1
<b>XC2</b>	Wet, rarely dry	Concrete surfaces subject to long-term water contact, many foundations	90-98	1	2
<b>XC3</b>	Moderate humidity	Concrete inside buildings with moderate or high air humidity, external concrete sheltered from rain	65-85	2	3
<b>XC4</b>	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2	85-90	2	3+

\* Risk: 0 = not significant, 1 = slight, 2 = medium, 3 = high, 3+ = maximum

For the *exposure class XC1 and dry environment* ( $45\% \leq RH < 65\%$ , mean value: 55%), carbonation is more rapid, actually for RH 50-60% the carbonation depth is maximum [33,77,83]. However, in this region the corrosion rate is slight due to still insufficient moisture for the corrosion cathodic process. According to Parrot [87], the critical corrosion depth of the reinforcing bar that causes visible deterioration is 100  $\mu\text{m}$ , and as the corrosion rate is about 0.3  $\mu\text{m}/\text{yr}$  [10,87] in this RH region, the propagation period is  $t_{\text{pr,carb}} > 100$  years. It has however to be noted that the predictions of Eq. (5.3.7) are more pessimistic giving a propagation period of the order of 40 years. Typical example of this case is the concrete inside buildings or structures where RH remains low during all service life.

For the same *exposure class XC1 but permanent wet environment* ( $RH \geq 98\%$ , mean value: 98%), carbonation is almost fully inhibited due to water-filled pores that decrease significantly the  $CO_2$  diffusion, and the corrosion process is also very slow for the same reason, as regards  $O_2$  diffusion. Typical examples of this case are concrete members that will be submerged at all times during the service life.

For the *exposure class XC2* (wet, rarely dry, in approximation  $90\% \leq RH < 98\%$ , mean value: 90%), both the carbonation and corrosion rates are greater than in the XC1 environment (permanent wet). Thus in this case corrosion rate is characterized as medium. Typical examples of this case include concrete reservoirs and water towers that will be full most of the time, and foundation or concrete members below ground level.

For the *exposure class XC3* (moderate humidity,  $65\% \leq RH < 85\%$ , mean value: 70%) carbonation is faster than XC2, and lower than XC1 (dry environment), characterized as medium. The corrosion rate is however at its high level due to presence of both oxygen and water. It is worthy noted that in such environment of high humidity the corrosion rate is rather fast, almost 5-20  $\mu\text{m}/\text{yr}$  [10,87], fact that gives propagation periods of the order of 5-20 years (as 100  $\mu\text{m}$  is the critical corrosion depth). Morinaga [86], through Eq. (5.3.7) estimates even shorter periods of 2 years! Typical examples of this case are external concrete surfaces sheltered from rain and internal concrete with higher than normal relative humidity (brewing industry, commercial laundries, etc). As these exposure conditions are rather common, and the corrosion rate is high enough, more onerous limiting values for concrete composition have to be applied, than those recommended by EN 206, as also proposed in British Standard BS 8500 [10,88].

For the last *exposure class XC4* (cyclic wet and dry, in approximation  $75\% \leq RH < 90\%$ , mean value: 80%) carbonation is still medium due to dry periods. The corrosion rate is at its maximum level due to presence of both oxygen and adequate water. It has also to be emphasized that concrete takes water in from the environment more rapidly than it loses it and thus the internal humidity could be higher than the average ambient humidity. This higher internal moisture speeds up the corrosion rate. Typical examples of this case are external concrete surfaces exposed to rain and many other mostly industrial applications.

## 5.4 Protection measures

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### 5.4.1 Protection against corrosion

The most effective protection measure against corrosion is the serious consideration of all corrosion parameters *at the design stage*. The most essential parameters are the environmental conditions, the designed service life, and the control methods [44]. Taking into account these parameters the engineer shall design the materials and the components composing the structure. With an adequate concrete cover and studied environmental actions, steel reinforcement in concrete cannot corrode up to the designed service life. Protection of the reinforcement from carbonation-initiated corrosion can be achieved by selecting the *concrete cover and the mix design* so that carbonation will not reach the bar surface within the expected lifetime of the structure. It has also to take in consideration that, at ambient temperatures, corrosion occurs *only if moisture is present*. Thus, surfaces should be exposed the lowest possible to moisture and they should dry out quickly, in order to prolong the service lifetime of the structure.

If however, corrosion is predicted to be unavoidable during the designed service life, several additional protection measures can be applied. A way to avoid corrosion is *to isolate concrete and/or reinforcement from the environment* that contains moisture. This would be done by applying one or more *protective coatings* to a suitably prepared surface. The case of coating application on concrete surface will be next analysed.

For reinforcement itself, some metallic coatings simply form a protective barrier (nickel, chromium, etc.) or are anodic materials compared to steel (zinc, aluminium, etc.) and thus provide a sacrificial protection. Organic coatings of different types (paints, pitch, tar, etc.) form a protective barrier, but they have to cooperate with concrete. In addition to sacrificial anodes, *cathodic protection* may be used, by the use of an external power source to make the metal cathodic to its environment. This method is costly and sometimes could be risky due to possible hydrogen evolution at the cathode, that can diffuse into the metal and embrittle it.

### 5.4.2 Protection by using waterproof sealants

The application of surface coatings to concrete has been proposed by many [85] as a means of reducing the rates of carbonation and corrosion. For example, Hankins [89] applied and examined more than 10 alternative coatings (among them a 6 mm thick layer of waterproof cement mortar) with respect to their effectiveness *as carbonation retarders*. Among these coatings only one, consisting of three brush-applied coats of soluble organic silicone resin or siloxane acrylic resins, and another consisting of three brush or roller applied coats of vinyl acetate copolymer or pure acrylic emulsion, were found effective in that respect. As another example [86] eight different surface coatings were tested as carbonation retarders. A vinyl wallpaper was found very effective, a cement mortar and a resin plaster were found fairly effective, whereas acrylic or epoxy-based spray finishes were less successful. Cement-based spray finishes or a lithium silicate surface hardener had almost no effect [86].

The above coatings may offer *impermeability* to concrete surface as respect water, decreasing thus dramatically the corrosion rate and in lesser degree the carbonation rate, e.g., carbonation is still at maximum rate for a low RH of 50% but corrosion is almost ceased. This can be translated in modelling terms as a decrease in the ambient relative humidity. The producer has to guarantee how much is this reduction and for how long it will last before the next serious coating repair.

Actually, because a strong gas-tightness is almost impossible to achieve at a reasonable cost, these materials decrease simply the diffusion process of CO<sub>2</sub>, O<sub>2</sub>, and water vapour. The higher their thickness and the lower their permeability, the lower the diffusion rate of detrimental agents. These concepts have been taken into account for modelling, using the more general case presented in the sequence, where in addition the coating may be act as a material arresting carbonation.

### 5.4.3 Protection by using cement-lime mortar coatings

#### a. Mathematical model

The mathematical model presented in section 5.2 was extended by Papadakis et al. [80] to cover the case of carbonation of the coating-concrete system, for concrete coated with a cement – lime mortar finish, applied either almost immediately after the end of concrete curing or with a delay of a certain time.

In many countries the ceiling and wall surfaces of most buildings are finished by covering them with plaster or render, a mixture of a cementing material, an inert fine aggregate, and water [90,91]. For interior surfaces the cementing material is sometimes gypsum or hydrated lime. Mixtures of cement and hydrated lime are used as cementing material for exterior or hard-usage surfaces, but also sometimes for interior ones. In what follows we will concentrate on this latter case, i.e., on the application of a lime-cement mortar coating and on its effect on the rate of carbonation. We will consider only lime produced by hydration of high-calcium quicklime, as that originating from the burning of limestone. Finally, in the following we will call dry hydrated lime, i.e.  $\text{Ca}(\text{OH})_2$  without excess water, simply “lime”.

The mathematical model of carbonation of concrete with a mortar coating is developed with reference to Fig. 5.4.1: superscripts (1) and (2) are used for plaster and for concrete, respectively. The thickness of the coating is denoted by  $d$  and the distance from the outer surface of the coating by  $x$ . The model applies to one-dimensional geometry, i.e., to concrete walls, slabs, beams or columns with planar external surfaces, with the exception of corner regions near the intersection of external surfaces, and of the vicinity of macroscopic cracks. A major hypothesis made is that the simplifying assumptions made for the carbonation of pozzolanic concrete or mortar, which have led to the formation of a carbonation front and to simple Eq. (5.2.1), can also be made for the carbonation of lime-cement mortar ( $\text{RH} > 55\%$ ). The carbonation depth, measured from the outer surface of the coating, is denoted by  $X_c$ , whereas that in concrete, measured from the coating-concrete interface, is still denoted by  $x_c$ .



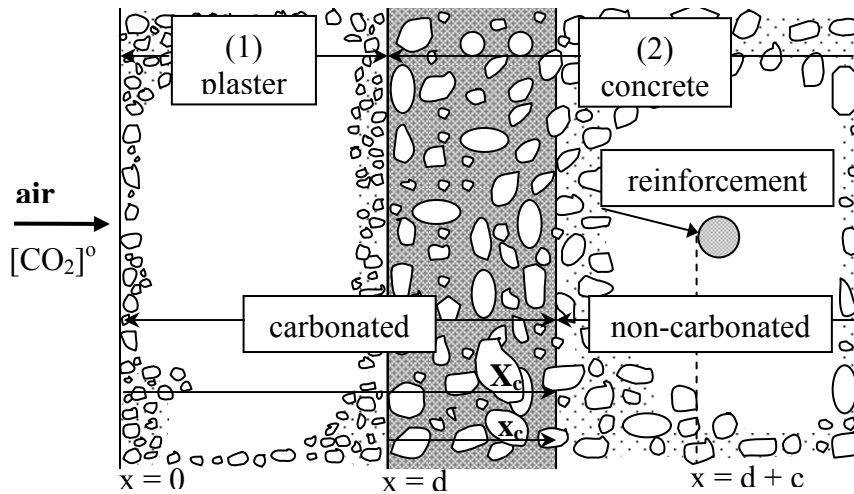


Figure 5.4.1 Schematic illustration of concrete carbonation in the presence of mortar coating ( $t > t_d$ ).

The carbonation of mortar-coated concrete consists of two phases. In the first, carbonation is limited to the coating and concrete remains unaffected. The end of this phase occurs at time  $t_d$  (at which carbonation depth equals  $d$ ), given by:

$$t_d = \frac{(0.33CH^{(1)} + 0.214CSH^{(1)})d^2}{2D_{e,CO_2}^{(1)}(CO_2/100)} \quad (5.4.1)$$

For  $RH < 55\%$  this time has to be corrected divided it by the factor  $\lambda^2$ , see section 5.2.2. So, during the first phase, i.e. for  $0 \leq t \leq t_d$ , the carbonation depth  $X_c$  in the coating is given by Eq. (5.2.1), with values of the parameters for the coating mortar, i.e. with superscript (1). During the second phase, i.e. for  $t > t_d$ ,  $CO_2$  is diffused according to the equation:

$$d^2[CO_2]/dx^2 = 0 \quad \text{for } 0 \leq x \leq X_c \quad (5.4.2)$$

within the coating ( $0 \leq x \leq d$ ), which is fully carbonated, and within the carbonated region of concrete ( $d \leq x \leq X_c$ ). By integrating Eq. (5.4.2), using appropriate boundary conditions, see [80], the carbonation depth  $x_c$  in the concrete measured from the interface is given by:

$$x_c = \sqrt{\frac{2D_{e,CO_2}^{(2)}(CO_2/100)}{0.33CH^{(2)} + 0.214CSH^{(2)}}(t - t_d) + d^2 \left( \frac{D_{e,CO_2}^{(2)}}{D_{e,CO_2}^{(1)}} \right)^2} - d \frac{D_{e,CO_2}^{(2)}}{D_{e,CO_2}^{(1)}} \quad (5.4.3)$$

From the Eq. (5.4.3) one can obtain the **critical time**,  $t_{cr,carb}$  (s), required for the carbonation front to reach the reinforcement located at a distance  $c$  (concrete cover, m) measured from the interface:

$$t_{cr,carb} = t_d + \frac{(0.33CH^{(2)} + 0.214CSH^{(2)})(c^2 + 2dcD_{e,CO_2}^{(2)} / D_{e,CO_2}^{(1)})}{2D_{e,CO_2}^{(2)}(CO_2/100)} \quad (5.4.4)$$

The above equations may be applied to predict the protection provided by a *simple coating*, that contains no cement or lime (thus  $CH^{(1)}=CSH^{(1)}=0$ ) and ensures only a lower permeability. In this case, the time  $t_d$  equals 0 and the effective diffusivity of  $CO_2$ ,  $D_{e,CO_2}^{(1)}$ , must be known.

In the above it has been assumed for analytical convenience that the mortar coating is applied almost immediately after the end of the concrete curing. In practice, however, a relatively long period of time, of the order of months, elapses between the end of concrete curing and the application of the finishing coat. In other cases, the concrete surface may be left initially uncoated, and after several years it may be decided to apply the finish, for reasons of architectural appearance, or for maintenance and protection from further deterioration. During the period of time, denoted by  $t_a$ , in which the concrete surface remains exposed to the environment, the concrete is left to carbonate and the carbonation front reaches a depth  $x_{c,a}$  obtained from Eq. (5.2.1) for  $t = t_a$  and for parameter values equal to those of the concrete (superscript (2)). Right after its application at time  $t_a$ , the coating mortar starts to carbonate according to Eq. (5.2.1), with the values of the parameters superscript by (1), until the carbonation depth in the coating reaches its thickness  $d$  at time  $t_d$ .

During this application of the protective outer layer it is possible dissolved  $Ca(OH)_2$  to diffuse in the carbonated areas of concrete from the neighbouring yet-uncarbonated areas. Since diffusion of very little quantity of dissolved CH is required for the equilibrium concentration of CH in water to be attained, the pH value in the already carbonated depth of concrete will go back to about 12.5 (re-alkalization), possibly passivating again the previously depassivated

bars (provided that corrosion has not yet started). However, as the total quantity of  $\text{Ca(OH)}_2$  in this previously carbonated concrete depth is very small, shortly after arrival of the carbonation front at the coating-concrete interface this total quantity of dissolved  $\text{Ca(OH)}_2$  will react with the new  $\text{CO}_2$  that diffuses in, and the carbonation front will jump to  $x_{c,a}$ . Then, the carbonation depth in the concrete, measured from the interface, is given by [80]:

$$x_c = \sqrt{\frac{2D_{e,\text{CO}_2}^{(2)}(\text{CO}_2/100)}{0.33CH^{(2)} + 0.214CSH^{(2)}}(t - t_d) + \left(d \frac{D_{e,\text{CO}_2}^{(2)}}{D_{e,\text{CO}_2}^{(1)}} + x_{c,a}\right)^2} - d \frac{D_{e,\text{CO}_2}^{(2)}}{D_{e,\text{CO}_2}^{(1)}} \quad (5.4.5)$$

and the time required for the carbonation front to reach the reinforcement is:

$$t_{cr,carb} = t_d + \frac{(0.33CH^{(2)} + 0.214CSH^{(2)})[c^2 + 2d(c - x_{c,a})D_{e,\text{CO}_2}^{(2)} / D_{e,\text{CO}_2}^{(1)} - x_{c,a}^2]}{2D_{e,\text{CO}_2}^{(2)}(\text{CO}_2/100)} \quad (5.4.6)$$

From parametric analyses presented elsewhere [80], it is shown that addition of a 20 mm thick layer of cement-lime mortar coating postpones the onset of carbonation in the concrete for more than 20 years (sometimes for 60 years or even longer). After which the advancement of carbonation within the concrete itself is much slower than during the initial period of carbonation of uncoated concrete, because  $\text{CO}_2$  has to diffuse through an additional 20 mm of mortar coating. Another interesting result is that even for very late application of the coating to initially exposed and already carbonated concrete turns out to be very effective technique for arresting carbonation.

#### *b. Mix design and physicochemical characteristics of the coating*

We suppose that the cement-lime mortar coating contains cement, lime, aggregates, water, and possibly additions and admixtures, i.e., all constituents that a typical concrete (mortar) contains plus lime. Thus, we follow the same mix design concept as applied in the concrete mix design (chapter 2), introducing only the new lime addition. We denote by  $L$  ( $\text{kg/m}^3$  mortar) the lime content in the mixture, defining as lime the dry  $\text{Ca(OH)}_2$  without excess water (in a water-saturated, surface-dry form), and by  $d_L$  the mass density of lime ( $\text{kg/m}^3$ ). The following mass balance equation has then to be fulfilled:

$$C/d_C + L/d_L + S/d_S + F/d_F + A/d_A + W/d_W + D/d_D + \varepsilon_{\text{air}} = 1 \quad (5.4.7)$$

The Eq. (5.4.7) may be used to calculate the *aggregate content* if all other composition parameters are known:

$$A = (1 - C/d_C - L/d_L - S/d_S - F/d_F - W/d_W - D/d_D - \varepsilon_{\text{air}}) d_A \quad (5.4.8)$$

The *water to cement ratio* ( $W/C$ ) is calculated as the ratio of the effective water content to cement content by mass in the fresh mortar. The *lime to cement ratio* ( $L/C$ ) is calculated as the ratio of the lime content to cement content by mass in the fresh mortar. The *aggregate to cement ratio* ( $A/C$ ) is calculated as the ratio of the aggregate content to cement content by mass in the fresh mortar. The *fresh mortar density*,  $d_{\text{MOR}}$  ( $\text{kg/m}^3$ ), is given by:

$$d_{\text{MOR}} = C + L + S + F + A + W + D \quad (5.4.9)$$

The  $\text{CH}^{(1)}$  and  $\text{CSH}^{(1)}$  contents and the porosity of carbonated mortar  $\varepsilon_c^{(1)}$  can be calculated using the expressions presented in chapter 2 for concrete. *The only difference is that in the amount of the calculated CH content, the lime content L should be added* (multiplied by the purity in CH). It is further assumed that the effective diffusivity of  $\text{CO}_2$  in a carbonated mortar coating,  $D_{e,\text{CO}_2}^{(1)}$ , can be computed from Eq. (5.2.2), which has been empirically fitted to a large data set derived from portland and pozzolanic mortar or concrete. Finally, the European Standard EN 998-2 [92] has to be followed in this case and the lime should conform to EN 459-1 [93].