Progresses in prevention of corrosion in concrete

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Abstract. Rebar corrosion, carbonation or chloride induced, is the most important cause of premature failure of reinforced concrete structures. Prevention of rebars corrosion is of paramount importance to reduce cost, increase reliability and improve sustainability of constructions. This goal can be achieved in design and construction stages by proper concrete mix (w/c ratio and cement type), suitable casting and curing procedures, sufficient concrete cover as a function of environment aggressiveness, according to standards as Eurocode and EN 206. Additional protection methods can be used in very aggressive environment or when very long service life is required. Among these methods, corrosion resistant reinforcements (galvanised or stainless steels), concrete coatings, corrosion inhibitors and cathodic prevention have been proposed in literature and applied in field. In the first part of the paper the most recent achievements of our research group on rebars corrosion prevention are examined. In the second part the evaluation of the initiation time of corrosion of a structure in severe environment exposed to chlorides is carried out by Monte Carlo simulation: the results show that cathodic prevention and stainless steels reinforcements are the most effective methods to guarantee a safe working condition of a reinforced concrete structure in a severe environment.

1. Introduction

Rebar corrosion is the most important cause of premature failure of reinforced concrete structures. This has been recognized during years '70 [1-4], while before reinforced concrete was considered as a material not subjected to degradation ("eternal"). The study of reinforcement corrosion in our Department dates back to years '80, thanks to Pietro Pedeferri. The activities of the research group lead by Pietro Pedeferri generated the publications of many research papers and books, both in Italian and in English [5-6].

1.1. Sustainability and durability of reinforced concrete structures

Many literature studies have shown that the cost of corrosion can reach about 4% of the GDP of industrial countries; of this cost about 1/5 (0.8% of GDP) could be saved by only applying the updated knowledge and available protection methods; as a consequence, corrosion prevention can contribute to reduce energy and raw materials consumption, making plants and constructions safer and more reliable [7].

Sustainability in the construction industry can be achieved through different approaches, with reductions in consumption of gross energy, polluting emissions, and nonrenewable natural resources.

Different strategies can be identified to make the concrete sector more sustainable: using alternative fuels and raw materials to reduce CO_2 emissions, replacing Portland cement with supplementary cementitious materials, reducing natural resource consumption through waste management and recycling [8]. It is well known from some decades that the use of pozzolanic or slag cements as a replacement for Portland cement can reduce both the energy consumption and the amount of waste, leading also in some cases to increased service life (see next chapter).

The reduction of the energy consumption is one of the most important contribution to improve the sustainability. Concerning corrosion prevention, it has been demonstrated that the application of cathodic protection for steel structures in soil and seawater is able to reduce significantly the overall energy consumption with respect to the energetic costs of material replacement [9-10].

The paper is focused on the prevention of rebars corrosion; by this way, it is also possible to reduce cost, increase reliability and improve sustainability of concrete sector. The paper is focused on the case of chloride induced corrosion that is the most aggressive phenomenon.

1.2. Corrosion of reinforcements in concrete

Normally carbon steel rebars in concrete are in passive condition, promoted by the alkalinity of concrete (pH higher than 12.6). Passivity can be destroyed and corrosion may occur, due to two main causes: carbonation of concrete, that is the reaction of atmospheric CO_2 with the cement paste that lowers the concrete pH; presence of chlorides at the rebar surface in a content higher than a critical value; although the definition of this threshold is not a simple task and its value depends on different parameters (among these the electrochemical potential of steel is the most important), its value for atmospherically exposed structures is generally in the range 0.4-1% by cement mass [5, 6, 11, 12]. Other two important phenomena can arise in specific conditions: hydrogen embrittlement of high strength steels and stray current corrosion: mainly the first of these can lead to premature failures [13-15].

Two phases can be identified in the service life of reinforced concrete structures subjected to corrosion, according to the Tuutti model [16]: the initiation of corrosion, during which CO_2 or chlorides penetrate the concrete cover, reaching the reinforcement and depassivating carbon steel, and the propagation phase, where corrosion takes place in presence of oxygen and water and can lead to serviceability limit state (concrete cracking or spalling, reduction of rebar cross section). The service life can be guaranteed by increasing both the initiation and the propagation time. In general, the increase of initiation time is more viable and reliable, and this is more evident in the case of chloride induced corrosion, since localised corrosion rate can be very high and propagation time very short [6].

2. Prevention of corrosion in concrete

The prevention of corrosion is primarily achieved in the design phase by using high quality concrete and adequate cover: this approach has been standardized in Eurocode 2 and EN 206 standard [17, 18, 19]. This is very important, because the majority of the corrosion damages are related to wrong design or bad execution (placing, compaction and curing of concrete).

Concerning the concrete quality, the beneficial effects of a low water-binder ratio on concrete permeability are well-known [6, 17, 19]. The cement type is also important: blast furnace slag and pozzolanic cement greatly reduce chlorides transport in concrete, provided the concrete is properly cured. For more recent alternative binders (sulfoaluminate cements, activated alkaline binders, geopolymers), the research has not yet fully established which are the improvements and limitations related to the prevention of corrosion and for this reason these binders will not be taken into consideration in this paper. An increase in the thickness of the cover increases the barrier to aggressive species, delaying corrosion initiation, but very high cover depth, more than 70-80 mm, is not realistic [6]. In relatively few but very important cases it may be necessary to increase the durability of the structure with appropriate preventative measures, often referred to as *additional protection system* [6, 20]. This happens in particular in the presence of very aggressive environment, mainly related to the presence of high concentrations of chlorides: marine structures, bridge decks, parking garages. These methods can also be used when it is impossible to obtain adequate cover thickness, as with very slender elements, when the structure is inaccessible for maintenance, or when the direct or indirect costs of future maintenance are extremely high.

2.1. Cathodic prevention

The application of cathodic protection (CP) to rebar in concrete dates back to the years ’70 and was initially referred to already corroding structures [5, 6, 21-28]. In the early 90s, Pietro Pedeferri proposed a special type of cathodic protection: it consists to polarize cathodically the passive rebars before corrosion initiation [22, 25]. This technique was named cathodic prevention (CPrev), to distinguish its peculiarities from those of cathodic protection [6]. The principle of cathodic prevention is based on the definition of localised corrosion initiation and repassivation, given by M Pourbaix [26]. Pitting (corrosion initiation) and repassivation potential of steel reinforcements in chloride containing concrete are shown in the diagram firstly proposed by Pietro Pedeferri [22] and later introduced in the EN ISO standard for CP in concrete [25] (Figure 1). Protection current density in the order of 1-3 mA/m^2, lower than the values applied to corroding rebars, produces a cathodic polarisation (potential reduction) of 100-200 mV, then enabling an increase in critical chloride content of one order of magnitude, i.e., more than 4% by cement weight [29].

Thank*s* to the experience gained in field *on* cathodic protection, it is possible to state that with a proper maintenance and monitoring system, CPrev is able to protect rebars from corrosion for the usual service life (50 years). Most of the applications of cathodic prevention refer to the use of impressed current technique [21, 22]. More recently the use of cathodic prevention by galvanic anodes has been proposed [30-31].

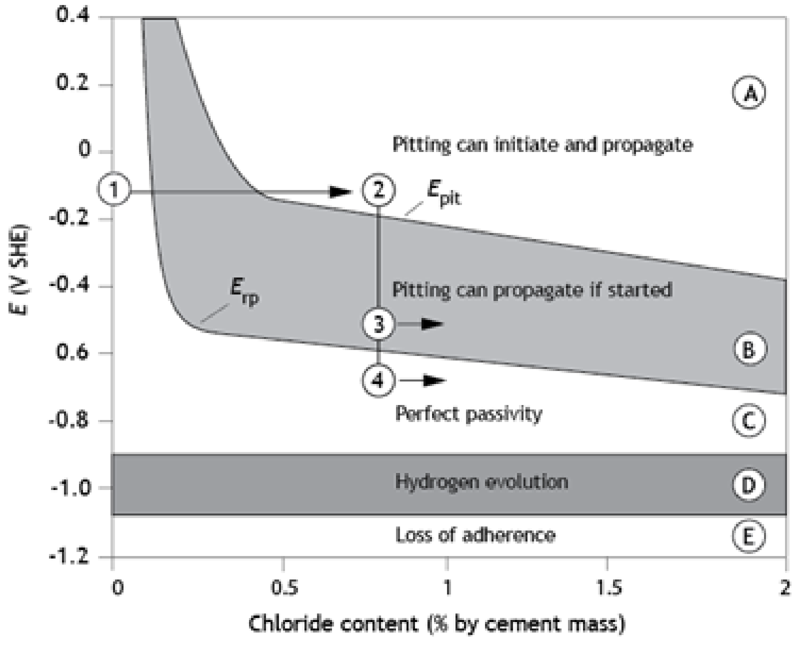

Figure 1. Pedeferri’s Diagram for corrosion initiation and propagation in concrete contaminated by chlorides, highlighting evolution paths of cathodic prevention [22, 25]

2.2. Surface protection systems

Four classes of surface treatments are available: organic coatings that form a continuous film, hydrophobic treatments, treatments that fill the capillary pores and cementitious layers [5-6]. The main action of coatings is to reduce the penetration of aggressive species and to increase initiation time, especially for chloride-induced corrosion [5-6]. Once corrosion has started, treatments able to stop water penetration may also reduce corrosion rate.

In literature many papers have characterized the behaviour of different coating types [32-36]. In our research group, we study the effect of polymer modified cementitious mortars [37-39]. These coatings are characterized by a good water vapour transport and crack bridging ability [5, 6, 32]. Two commercial cementitious coatings, modified with acrylic-based polymer and polymer-to-cement (p/c) ratio of 0.35 and 0.55, mean thickness 2 mm, have been tested. The initiation of corrosion was significantly delayed in presence of coatings, as can be seen in Figure 2 [39]. This effect was mainly attributed to the reduction of chloride transport in concrete [39]. The protective effect is more pronounced as the polymer content (p/c) increases. After corrosion initiation, in coated concrete, corrosion rate is reduced due to the lower water content in concrete, even if this effect is less important. As expected, no effect on the critical chloride threshold has been found.

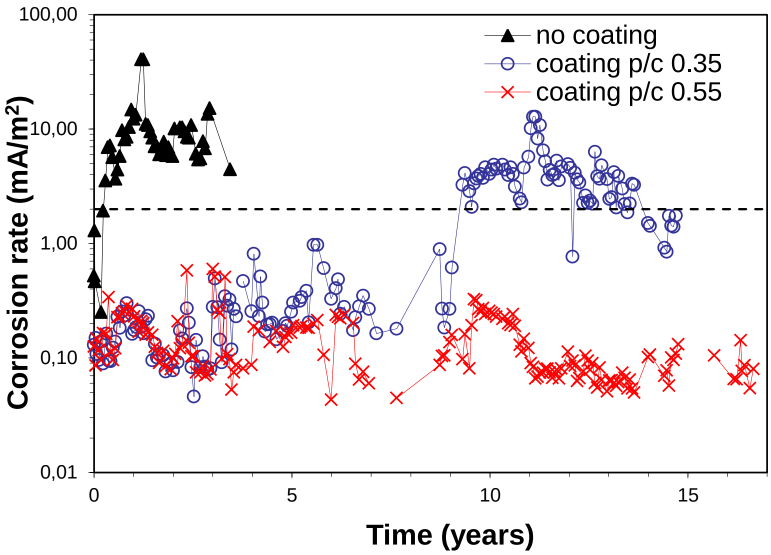

Figure 2. Rebars corrosion rate in concrete (coated and not) subjected to chloride ponding [39]

2.3. Corrosion inhibitors

Corrosion inhibitors seem to offer a simple and cost-effective prevention technique. They may be used both as a preventative technique, if added to fresh concrete, and as a repair system, if applied on hardened concrete [6, 40]. Only the first approach is considered here.

Nitrite based inhibitors were studied since the late 50s [40-42], while organic inhibitors, based on blends of alkanolamines, amines or amino-acids, have been proposed in 80s [40, 43-45]. In proper concentration, some inhibitors can delay the initiation of corrosion, due to the higher critical chloride content: 1-1.5% by cement mass for organic corrosion inhibitors and variable, proportional to the dosage, for nitrite-based inhibitors: with the highest dosage the critical chloride content can be 2% or more.

In more recent years also new substances or mixture have been studied as a possible alternative to commercial corrosion inhibitors [46-48]. In our research group the performance of corrosion inhibitors (both commercial and organic substances or mixtures) for reinforced concrete structures affected by chloride induced and carbonation corrosion has been studied in the last 15 years [49-53].

The results obtained in our research with nitrite-based inhibitor confirm literature data: the inhibitor is effective if the molar ratio $[NO_2^-]/[Cl^-]$ is higher than 0.5-0.6. Organic commercial admixed corrosion inhibitors delayed the occurrence of chloride induced corrosion; this result is related mostly to the reduction of the chloride transport rate into concrete rather than an increase of the critical chloride threshold. Among the tested organic substances, compounds containing carboxylic group showed the best results in simulated pore solution tests: critical chloride content are similar to those obtained with sodium nitrite. In concrete tests, only one amine and one amino acid showed good performance increasing the critical chlorides threshold with respect to the reference condition (Figure 3). The performance of the organic mixtures was not satisfactory.

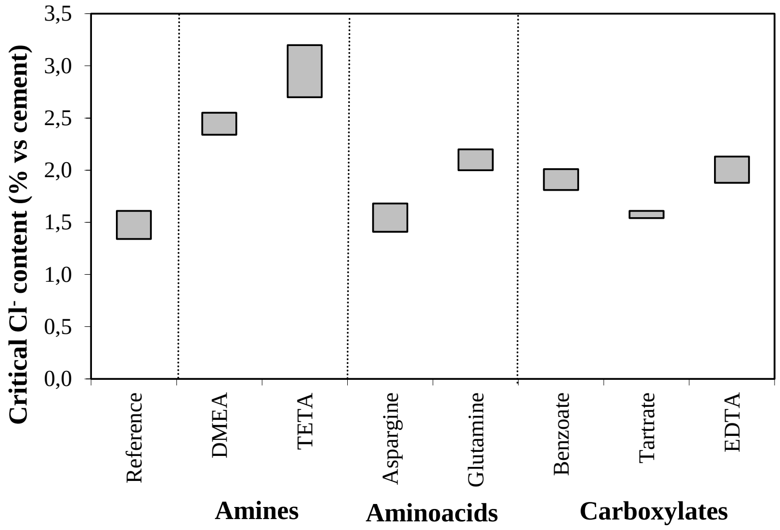

Figure 3. Performance of different corrosion inhibitors in concrete subjected to chloride ponding [52]

2.4. Corrosion resistant reinforcements

Stainless steels are able to significantly increase the critical chloride content vs carbon steel. They have proven to be effective in preventing corrosion even under very aggressive conditions, both in laboratories and in field exposure; this is the case of the Progreso bridge in Mexico built more than 80 years ago [6]. Starting from the 80s, a wide range of stainless steels and exposure conditions were investigated [6, 54-55]. Traditional austenitic steels 1.4307 and 1.4404 (both with 18% Cr and 8% Ni, the 2nd with 2-3% Mo) or duplex stainless steel type 1.4462 (22% Cr and 5% Ni, plus 3% Mo) can be safely used in alkaline concrete: they guarantee an important increase in the critical chloride content, up to 5% by cement weight (Figure 4). These chloride values are rarely reached at the steel surface, then stainless steel bars can been used to guarantee an extremely long service life. Moreover, the risk of galvanic coupling corrosion has been demonstrated to be negligible [56].

Galvanised steel has been studied extensively in laboratory, while the field applications are not very numerous. They provide an increase of the critical chloride content vs carbon steel rebars up to 1.5% by cement mass, not comparable to the performance of stainless steel reinforcements [57-59]. As far as the epoxy coated rebars are concerned, despite the lon term studies their effectiveness in chloride contaminated concrete is a conflicting topic, while they can be more effective in carbonated concrete [6].

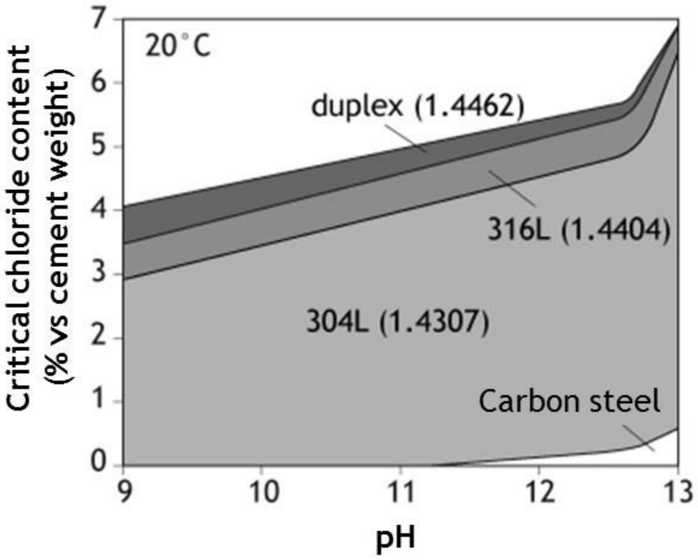

Figure 4. Schematic field of applicability for different type of stainless steels at 20°C [6]

3. Service life design

As already said, the use of prescriptive approach according to EN 206 and Eurocode 2 [17-18], i.e. maximum w/c ratio, minimum cover thickness depending on the aggressiveness of the environment, would eliminate most of corrosion cases, for the usual service life of 50 years.

Performance based approach can provide much more information, especially the probabilistic ones. Deterministic approach is of limited use: if average value of the parameters are considered, also service life prediction would be an average value, which corresponds to high and unacceptable failure probability (50% approximately). Probabilistic performance-based approaches are able to take into account the intrinsic variability of the influencing factors. This approach has been implemented in different models, among these probably the most relevant one is the Model code for service life design [60], issued by the International Federation for Concrete (fib) in 2006. The code models the effect of environment on the structure and evaluate the probability that a defined limit state (initiation of corrosion, concrete cracking or spalling) is reached. Nowadays, the use of this model is limited since a few number of structures were designed in agreement with the model and a comparison between the predictions and the real performance is not easy [61-64]. Moreover, the model does not provide sufficient indications for the determination of some input parameters, in particular the surface chloride concentration, the critical chloride content for rebars different from carbon steel [64]. Also the definition of chloride diffusion coefficient with short term measurements and "aging" coefficients is discussed. In literature there are other probabilistic models focused on the evaluation of Life cycle cost and optimization of the maintenance [65-69].

The application of a probabilistic performance-based approach, simpler than FIB Model Code, is proposed in this paper. Monte Carlo simulation was applied to evaluate the initiation time of chloride-induced corrosion. The complete results of these analyses are reported in previous papers [70-71], here the methodology and main results are summarized.

3.1. Modeling durability

In the case of chloride-induced corrosion, chloride transport is mainly due to diffusion and capillary sorption. Mario Collepardi in 1972 was the first to propose the solution of 2nd Fick's law of diffusion for the interpolation of experimental chloride profiles [72]. The 2nd Fick's law is analogous to the 2nd

Fourier law for thermal diffusion, where the concentration gradient takes the place of temperature gradient and mass diffusion coefficient takes the place of thermal diffusivity.

Assuming the chlorides content at the concrete surface (C_s) constant with time, considering an apparent chloride diffusion coefficient (D_{app}) constant in time and space (i.e. concrete is homogeneous), and a semi-infinite diffusion length, the analytical solution of the 2nd Fick's law is:

$$C_x = C_S \cdot (1 - erf \frac{x}{2\sqrt{D_{app} t}}) \quad (1)$$

where erf is the error function, C_x is the chloride content at the depth x and t is time [6, 72] and the initial chloride content in concrete ($C_{x,t=0}$ for x>0) has been fixed equal to 0.

Even though the use of this equation received many discussions in the literature, and the analytical solution is based on some simplified assumption, the results are considered sufficiently accurate if proper values of the input parameters are selected. Based on the Equation 1, the initiation time of corrosion t_i is evaluated when, at the rebar surface i.e. x = *d* (cover depth), the chloride content ($C_{x=d}$) is equal to the critical chloride threshold ($C_{critical}$).

The failure probability (P_f) is evaluated as the probability that a limit state is reached. In this paper the limit state corresponds to corrosion initiation: this is a conservative approach, taking into account that the chloride induced corrosion is localized and the propagation period of corrosion could be very short [6]. Other limit state, as concrete cracking or spalling could be considered.

The evaluation of the distribution of the service life need the definition of the distribution of the influencing parameters, considered as random variables: surface chloride content (C_s), apparent chloride diffusion coefficient D_{app}, critical chloride content ($C_{critical}$) and concrete cover (*d*). The distribution with mean value and standard deviation are reported in Table 1, 2 and 3; when possible, parameters have been selected according the fib Model Code [60], in the other cases a brief explanation is reported based on literature and tests performed in our labs.

Exposure classes have been selected according to EN 206 [18]: atmospheric marine (XS1) and splash/tidal zone (XS3). Water/cement ratio 0.45 has been selected according to EN 206 for the most severe exposure. Two types of cement has been considered: CEM I (Ordinary Portland Cement) and CEM III (blast furnace slag) according to the EN 197 standard [73]. The preventative measures considered are: corrosion inhibitor, concrete coating and stainless steel AISI 304.

Cathodic prevention is used as reference: in fact, if properly applied it is able to tolerate a very high chloride content and so corrosion never initiate, provided monitoring and maintenance of the system (current feeder, connection cables or anodes) are properly scheduled and performed. In practice, only failures of the system for long time can provoke the onset of corrosion.

3.1.1. Surface chloride content

No clear indication are given in the fib Model Code, so distribution has been selected based on literature. For the exposure class XS3 the values suggested in the paper [64] are considered; for the exposure class XS1 the values were halved (Table 1). In the presence of coatings, the chloride concentration at the concrete surface is reduced as follow, according to a 17-year long experimentation conducted at PoliLaPP [38-39]: mean value 3% and standard deviation 1.2% in zone XS3; mean value 1.5% and standard deviation 0.6% in zone XS1.

3.1.2. Cover depth

Normal distribution has been selected according to fib Model Code: two mean values were selected for each exposure class, i.e. the minimum suggested by the standard and an increased value (Table 1), while the standard deviation was 10 mm [64].

3.1.3. Chloride diffusion coefficient

The mean values hsve been selected based on literature, considering long term measurements for concrete with w/c ratio 0.45 and manufactured with CEM I or CEM III. Lognormal distribution have been selected (Table 2). In presence of the coating, diffusion coefficient is reduced by 30%, according to [38, 39].

3.1.4. Critical chloride threshold

For carbon steel rebar, in agreement with the fib Model Code, Beta distribution with mean value 0.6% by cement mass and standard deviation 0.15% has been selected. Since no information are available in the fib Model Code, for the preventative techniques the same distribution has been used, with different mean values and standard deviation, mainly based on literature [6, 40, 49-53, 63]. Table 3 reports all values.

Table 1. Surface chloride content (C_s) and cover depth (*d*) used for the Monte Carlo simulation

		Marine exposure, atmospheric (XS1)		Marine exposure, splash/tidal (XS3)	
C_s [% by cement mass]	*Mean value*	2.5%		5%	
Lognormal distribution	*Std deviation*	1%		2%	
d [cm]	*Mean value*	35	45	45	60
Normal distribution	*Std deviation*	10	10	10	10

Table 2. Diffusion coefficient (D_{app}) used for Monte Carlo simulation (concrete w/c 0.45)

		CEM I		CEM III
		No coating	Coating	No coating
D_{app} [$10^{-12}m^2/s$]	*Mean value*	1	0.7	0.2
Lognormal distribution	*Std deviation*	0.2	0.14	0.04

Table 3. Critical chloride threshold ($C_{critical}$) used for Monte Carlo simulation

		Carbon steel	**Stainless steel AISI 304**	**Corrosion inhibitor**
$C_{critical}$ [% by cement mass]	*Mean value*	0.6	5	1.2
Beta distribution	*Std deviation*	0.15	1.25	0.3

4. Service life results

Initiation time of corrosion is calculated by means of Eq. 1. Values of relevant factors (surface and critical chloride content, diffusion coefficient, cover) are obtained by means of extraction of random numbers in a homemade program in Microsoft Excel©. The probability distribution of service life is obtained by Monte Carlo simulation after 1000 run of the program and the different technical solutions can be compared.

Results hereafter presented must be considered as an indication and not a solution valid in every similar situation. In a real case, the parameters of the distributions used to characterize the performance of concrete, rebars and environment may vary according to the design and execution of the structure [65-69].

Figures 5-8 report the results of the Monte Carlo simulation for the exposure class XS3 and XS1, respectively. The horizontal dotted line corresponds to 10% failure probability, which can be considered a target value as suggested by fib Model Code [60]. The vertical line corresponds to the target lifetime 50 years according to Eurocode 2 [19] for common structures (buildings), while 100 years, maximum of the service life range, is the target for bridges and infrastructures.

For aggressive conditions (exposure class XS3) it is evident that carbon steel rebar in concrete cast with Portland cement (CEM I) and w/c 0.45 as suggested by the EN 206 [18] is not a reliable option, for both the considered cover, 45 mm and 60 mm, the first corresponding to the value suggested by the Eurocode 2 [19]. In both cases, the 10% failure probability is reached in few years. At 50 years' service life, failure probability is higher than 80%. The prescriptions of the standards EN 206 and Eurocode 2 seem not to be adequate in such severe condition. The performance slightly improves with the use of corrosion inhibitors, that approximately double the critical chloride content. These results can be extended to the use of galvanized steel, characterized by a similar distribution of the critical chloride content [6]. Performance of concrete coating is similar to corrosion inhibitors, taking into account that maintenance of the coating itself is necessary every maximum 20 years, and this operation would increase the overall cost of this solution.

The use of CEM III improves the performance. In severe conditions (XS3), failure probability is lower than 10% for at least 50 years, if the cover is 60 mm. In less severe conditions (XS1) the same durability can be achieved with 45 mm cover. Combining the use of CEM III with corrosion inhibitors in severe exposure (XS3) the failure probability is lowered below 10% at 50 years with mean cover 45 mm. The reliability of this solution requires the stability of corrosion inhibition and the absence of leaching: this could be the case of cracked concrete.

The best performance is reached with stainless steel 1.4307: in severe conditions (XS3) failure probability remains lower than 10% for at least 80 years if the mean cover depth is 45 mm, more than 100 years if the mean cover depth is 60 mm. By combining stainless steel with concrete cast with CEM III the performance could be improved even more.

Typically, the use of stainless steel is limited by the high investment cost; nevertheless, costs can be reduced by a selective use of stainless steel limited to the more vulnerable parts of the reinforced concrete structure. No risk of galvanic corrosion with carbon steel rebars has been demonstrated [56]. In this paper we have not approached the analysis of the Life Cycle Cost (LCC); as a first approximation, even though both stainless steel reinforcements and cathodic prevention increase significantly the investment costs, from the service life results it can be deduced that they decrease significantly the repair and maintenance costs. In some literature paper the results of the life cycle cost are different [67-68]. It has to be mentioned that some hypothesis in these papers are significantly different: the duration of the cathodic protection systems is considered quite low (12.5 years) or the performances of traditional repair systems or other preventative methods like epoxy coated rebars seems overestimated. This brief discussion about the Life Cycle Cost cannot be considered exhaustive and require further work, together with the evaluation of the environmental impact of reinforced concrete structures subjected to corrosion, by Life Cycle Analysis or similar methods. This topic has received little attention in the literature.

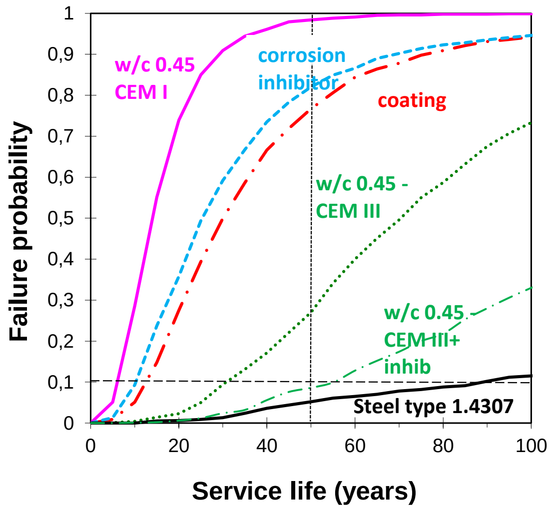

Figure 5. Cumulative distribution of the service life: exposure class XS3, mean cover 45 mm

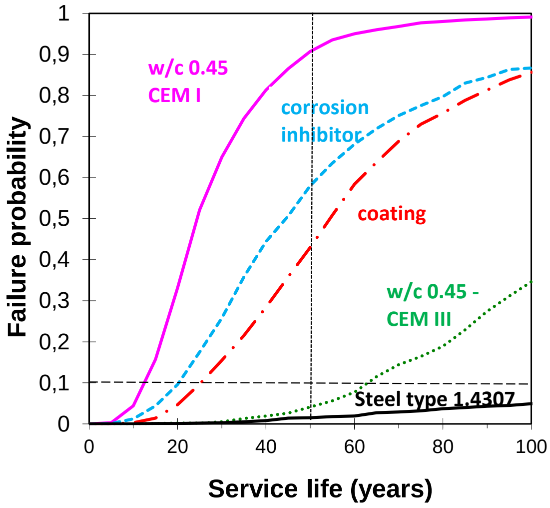

Figure 6. Cumulative distribution of the service life: exposure class XS3, mean cover 60 mm

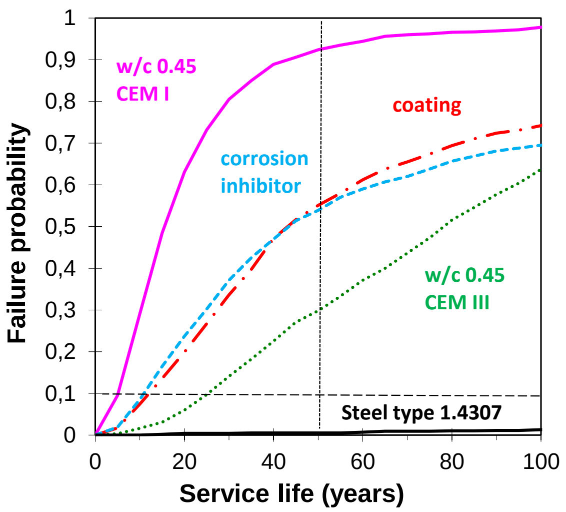

Figure 7. Cumulative distribution of the service life: exposure class XS1, mean cover 35 mm

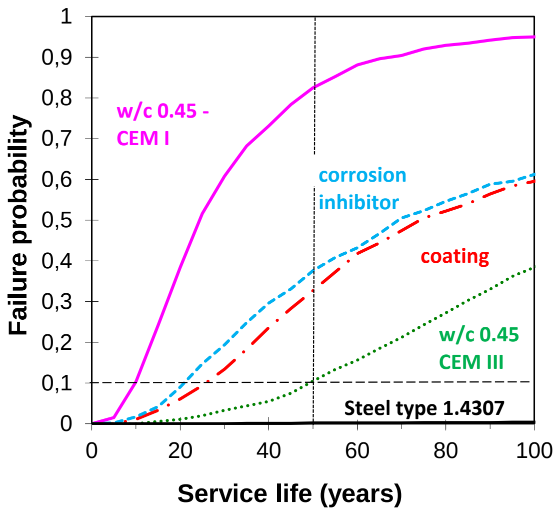

Figure 8. Cumulative distribution of the service life: exposure class XS1, mean cover 45 mm

5. Conclusions

In the paper, after a review of the experimental results obtained in our research group on the rebar corrosion prevention methods, a probabilistic performance-based approach have been applied to compare their performances. The approach used in this paper is simpler with respect the fib Model Code and requires a lower number of input parameters.

In severe conditions, as in splash/tidal zone of marine structures, only the use of stainless steel rebars and cathodic prevention can guarantee a low failure probability for the target service life (50 years or more). Corrosion inhibitors and coatings do not show a relevant effect on the service life. In concrete cast with low w/c ratio, blast furnace slag cement and high cover depth (60 mm instead of 45 mm suggested by Eurocode) failure probability remain below 10% for the target life 50 years.

In less severe environment (atmospheric marine), the failure probability decreases; only stainless steels rebar are able to guarantee a low failure probability for 50 years' service life for the suggested w/c ratio and cover. Increasing the cover, concrete cast with CEM III is able to maintain low failure probability during service life 50 years, while the use of corrosion inhibitors and coatings are not enough effective; nevertheless, these methods are able to delay the repair or reduce the number of interventions: this effect can positively influence the Life Cycle Cost.

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