1. MECHANISMS OF CONCRETE DETERIORATION

1.1 Background

Concrete is the most widely used building material. Its good performance in service, including *durability*, is the second important characteristic after the usual required mechanical properties. However, the last decades the problems of unsatisfactory durability of structures, especially reinforced concrete ones, are in a dramatic increase. This causes not only *economic impacts*, because the repairing expenses of deteriorated structures are almost equal to the cost of construction of new ones, but also *industrial, environmental and social problems* due to decrease of reliability and safety, see Fig. 1.1.1. Since the state-of-the-art of concrete durability has enjoyed a relatively short research history compared to strength; durability has replaced strength as the number one issue concerning the engineering community today [1-6].

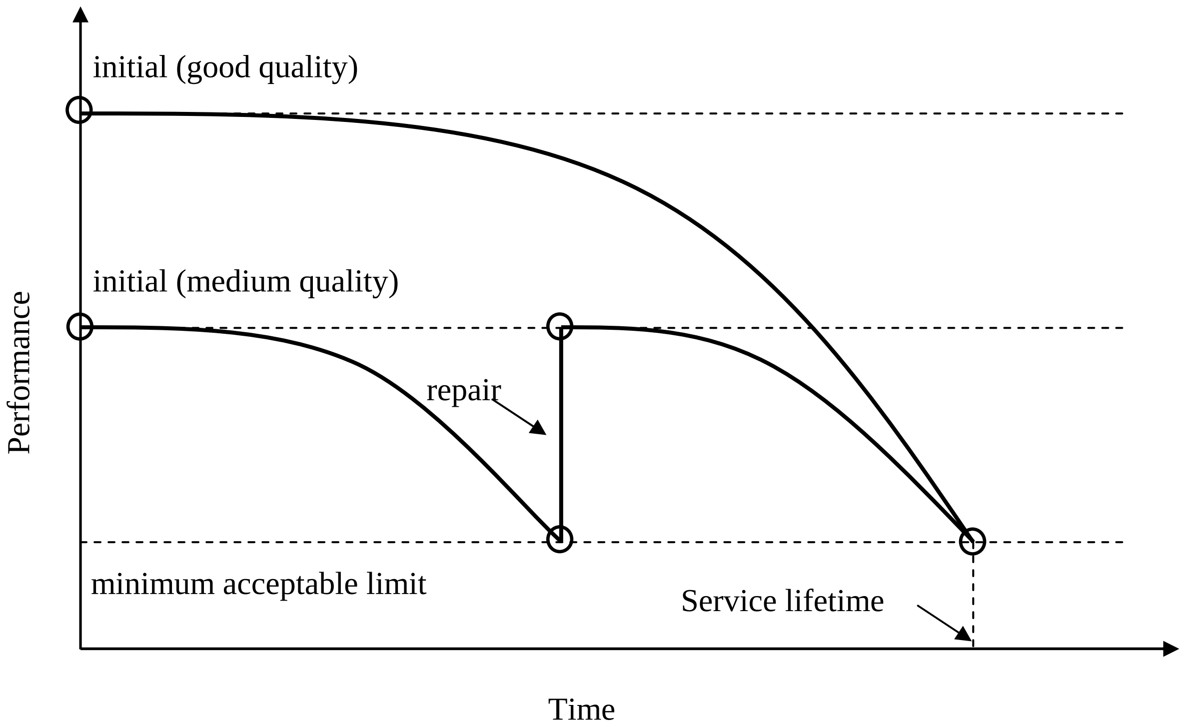

Figure 1.1.1 Relationship between concrete performance and service life.

The type and rate of degradation processes for concrete and reinforcement determines the resistance and the rigidity of the materials, the sections and the elements making up the structure. This reflects in the *safety*, the *serviceability* and the *appearance* of a structure, i.e., determines the ***performance of the structure***. ***Concrete working life or service lifetime*** is the period of time during which the performance of the concrete structure will be kept at a level compatible with the fulfilment of the performance requirements of the structure, provided it is properly maintained. As observed in Fig. 1.1.1, this service life may be achieved either due to initial good quality, or due to repeated repair of a not so good structure. The modeling of the deterioration mechanisms and the quantitative approach of the service life is the main objective of the present work.

As ***durability*** of a structure called the ability to resist against environmental attacks without its performance to drop below a minimum acceptable limit. Three following main factors define the concrete durability: the *initial mix design* (quality and relevant quantity of the concrete constituents), *structure* design, construction and maintenance, and the specific *environmental conditions.*

Deterioration of building materials in service is every loss of performance, and it may be the result of a variety *of mechanical, physical, chemical or biological processes*. Concrete (and cement products in general) is also susceptible to all these types of deterioration [5-11]. The final result of these mechanisms is mainly *cracking*. Cracking will occur whenever the tensile strain to which concrete is subjected exceeds the tensile strain capacity of the concrete.

As <u>*mechanical processes*</u> causing cracking can be considered the plastic shrinkage, the plastic settlement, the direct loading, and the imposed deformations:

- *Plastic shrinkage* is caused by capillary tension in pore water when the water loss by vaporization exceeds the supply by bleeding water (mainly map surface cracking).
- If *settlement* of concrete is hampered by the reinforcement or by the formwork, cracking can, also, occur (longitudinal cracks).
- Cracking caused by *direct loading* is the result of normal load effects (i.e., bending, shear, tension, etc.) applied to sections.
- As *imposed deformations* causing cracking can be considered differential settlement of foundations, earthquakes and other natural catastrophes.

- A mechanical process causing deterioration of the surface is the *erosion either by abrasion or cavitation.*

Concrete cracking due to the reinforcement corrosion (and creation of internal expansion tensions) will be included in the chemical processes, because these are responsible for the corrosion.

As *physical processes* causing cracking can be considered the temperature differences, the shrinkage, and the frost action:

- One of the major causes of cracking is movement resulting from the cooling of members from the *temperatures* generated by hydration of cement during a specific use of concrete.
- *Shrinkage* is the load independent, long-term deformation of concrete because of its decrease in volume due to drying.
- In the case of *water freezing* in concrete, the following physical processes are of major importance: Transition from water to ice involves an increase in volume by 9% and the freezing point is depressed as the pore diameter decreases. In the case of completely water-filled pores such expansion will cause splitting of concrete. Owing to this fact, a sufficient quantity of pores not filled with water shall be available.

The *chemical processes* causing concrete deterioration can be divided into two categories according to the medium they influence: *concrete or reinforcement*:

In the first category belongs the chemical attack *of aggressive substances* (ions and molecules) on concrete. A precondition for chemical reactions to take place within the concrete is the presence of water in some form (liquid, vapor). In general, the reactions between the aggressive substance (present in the concrete or transported from the environment) and the reactive substance of the concrete take place as they meet each other. However, often because of the low rate of transport of these substances, these reactions may take many years to show their detrimental effect. For practice, the most important chemical attacks on concrete are the acid, the sulphate and the alkali attack:

- The *action of acids* (as well ammonium salts, magnesium salts, and soft water) on the hardened concrete is practically a conversion of all the calcium compounds to the calcium salts of the attacking acid. These salts are very soluble and can be removed by dissolution or abrasion destroying the binding capacity of the cement.

- *Sulphate attack* on concrete is the reaction of sulphate ions with the aluminate phase of the cement, which causes expansion of the concrete, leading to cracking and disintegration.
- In the case of the *alkali attack*, alkalis from the cement present in the pore solution can react with silica containing aggregates resulting in the formation of alkali-silica gel (alkali- aggregate reaction). This may lead to destructive expansion if enough water is present, starting with small surface cracks and followed eventually by complete disintegration.

Reinforcing bars in concrete are protected from corrosion by a thin oxide layer that forms on their surface due to high alkalinity, i.e., the high pH-value, of the surrounding concrete. *Corrosion* may start when this protective layer is destroyed:

- either by *chloride penetration* (and the chloride content exceeds a critical value),
- or due to a reduction in the pH value of concrete to values below 9. Such a reduction in alkalinity is the result of *carbonation* of the $Ca(OH)_2$ in the concrete mass, i.e., of its reaction with the atmospheric CO_2 that diffuses through the concrete pores.

In marine or coastal environments, and when deicing salts come in contact with the concrete surface, chloride penetration is the main mechanism that paves the way to initiation of reinforcement corrosion. In all other cases, and especially in CO_2-rich urban and industrial areas, carbonation of concrete is the main mechanism leading to steel corrosion. Furthermore, the two mechanisms are synergetic, i.e., chloride action is accelerated by carbonation. However, corrosion of the reinforcement is possible, *if sufficient moisture and oxygen are available*.

Finally, many *biological processes*, such as *growth* on concrete structures may lead to mechanical deterioration caused by lichen, moss, algae and roots of plants:

- *Microgrowth* may cause chemical attacks by developing humic acid, which dissolves the cement paste.
- In practice, the most important type of biological attack occurs in sewer systems, where *hydrogen sulfide* (formed during anaerobic conditions) may be oxidized by bacteriological action to form sulfuric acid, thus resulting in an acid attack on concrete.

Fig. 1.1.2 summarises various possible causes of concrete deterioration and gives some indication of the age at which the various forms of cracking can be expected to occur.

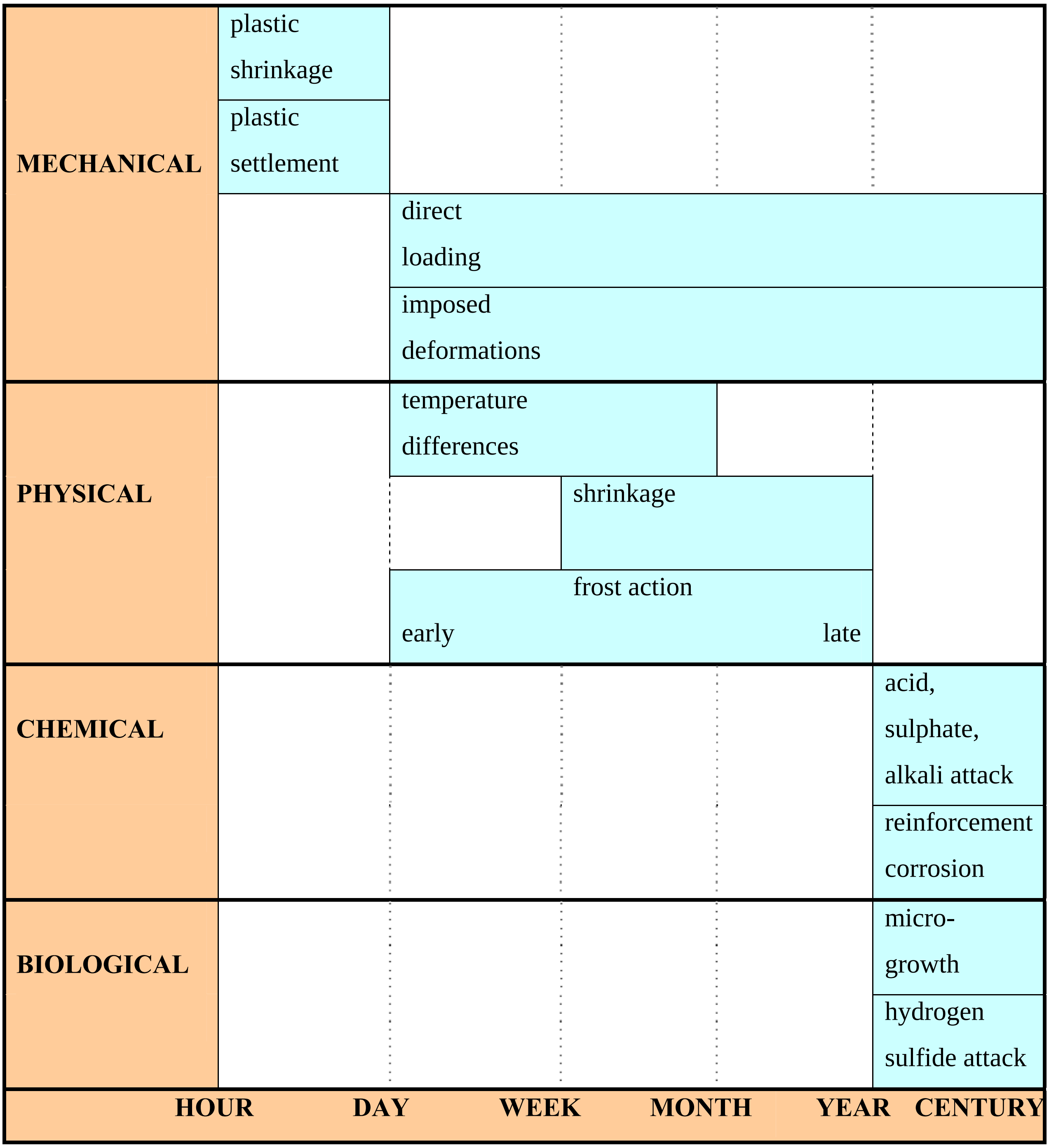

Figure 1.1.2 Deterioration mechanisms and most possible time of appearance of cracking.

1.2 The European Standard EN 206 and durability aspects

The *European Standard EN 206* [12], prepared by Technical Committee CEN/TC 104 "Concrete and related products", specifies requirements for the constituents materials of concrete, the properties of fresh and hardened concrete and their verification, the limitations for concrete composition, the specification of concrete, the delivery of fresh concrete, the production control procedure, the conformity criteria and evaluation of conformity. It applies to concrete for structures cast in situ, precast structures, and structural precast products for buildings and civil engineering structures. The concrete may be mixed on site or ready-mixed. It defines tasks for the specifier, producer and user. The *specifier* is responsible for the specification of the concrete, the *producer* for the conformity and production control and the *user* for placing the concrete in the structure.

The EN 206 is applied in Europe under different climatic and geographical conditions, different levels of protection and under different regional traditions and experience. Classes for concrete properties have been introduced to cover these situations. During the development of this European Standard, consideration was given to detailing a *performance-related approach to the specification of durability*. The committee CEN/TC 104 concluded that test methods to specify durability are not yet sufficiently developed to include them in the standard. However, this standard permits the continuation and development of performance-related methods for assessing durability, *as the present work does*. Development of EN 206, and the relevant parts of design code Eurocode 2 such as cover to reinforcement, provided for the first time matters of specification and design for durability.

According to EN 206, *environmental actions* are those chemical and physical actions to which the concrete is exposed and which result in effects on the concrete or reinforcement or embedded metal that are not considered as loads in structural design. The main deterioration actions considered are corrosion of reinforcement induced either by carbonation or chlorides, freeze/thaw and chemical attack. This has been framed in an exposure classification system. The environmental actions are classified as ***exposure classes*** and presented in Table 1.2.1. The exposure classes to be selected depend on the provisions valid in the place of use of the concrete.

Table 1.2.1 Exposure classes according to European Standard EN 206.

Class	Description of the environment	Informative examples
1 No risk of corrosion or attack		
X0	For concrete without reinforcement or embedded metal: All exposures except where there is freeze/thaw, abrasion or chemical attack For concrete with reinforcement or embedded metal: Very dry	 Concrete inside buildings with very low air humidity
2 Corrosion induced by carbonation		
Where concrete containing reinforcement or other embedded metal is exposed to air and moisture, the exposure shall be classified as follows:		
XC1	Dry or permanent wet	Concrete inside buildings with low air humidity, concrete permanently submerged in water
XC2	Wet, rarely dry	Concrete surfaces subject to long-term water contact, many foundations
XC3	Moderate humidity	Concrete inside buildings with moderate or high air humidity, external concrete sheltered from rain
XC4	Cyclic wet and dry	Concrete surfaces subject to water contact, not within exposure class XC2
3 Corrosion induced by chlorides other than from sea water		
Where concrete containing reinforcement or other embedded metal is subjected to contact with water containing chlorides including de-icing salts, from sources other than from sea water, the exposure shall be classified as follows:		
XD1	Moderate humidity	Concrete surfaces exposed to airborne chlorides
XD2	Wet, rarely dry	Swimming pools, concrete exposed to industrial waters containing chlorides
XD3	Cyclic wet and dry	Parts of bridges exposed to spray containing chlorides, pavements, car park slabs
4 Corrosion induced by chlorides from sea water		
Where concrete containing reinforcement or other embedded metal is subjected to contact with chlorides from sea water or air carrying salt originating from sea water, the exposure shall be classified as follows:		
XS1	Exposed to airborne salt but not in direct contact with sea water	Structures near to or on the coast
XS2	Permanently submerged	Parts of marine structure
XS3	Tidal, splash and spray zones	Parts of marine structure

Table 1.2.1 (continued)

Class	Description of the environment	Informative examples
5 Freeze/thaw attack with or without de-icing agents		
Where concrete is exposed to significant attack by freeze/thaw cycles whilst wet, the exposure shall be classified as follows:		
XF1	Moderate water saturation, without de-icing agent	Vertical concrete surfaces exposed to rain and freezing
XF2	Moderate water saturation, with de-icing agent	Vertical concrete surfaces of road structure exposed to freezing and airborne de-icing salts
XF3	High water saturation, without de-icing agent	Horizontal concrete surfaces exposed to rain and freezing
XF4	High water saturation, with de-icing agent or sea water	Road and bridge decks exposed to de-icing agents. Concrete surfaces exposed to direct spray containing de-icing agents and freezing. Splash zones of marine structures exposed to freezing
6 Chemical attack		
Where concrete is exposed to chemical attack from natural soils and ground water as given in Table 1.2.2, the exposure shall be classified as given below.		
XA1	Slightly aggressive chemical environment according to Table 1.2.2	
XA2	Moderately aggressive chemical environment according to Table 1.2.2	
XA3	Highly aggressive chemical environment according to Table 1.2.2	

The concrete may be subject to more than one of these actions and the environmental conditions may need to be expressed as a combination of exposure classes. The *aggressive chemical environments*, classified in Table 1.2.2, are based on natural soil and ground water at water/soil temperatures between 5-25 ^{o}C and a water velocity sufficiently to approximate to static conditions. The most onerous value for any single chemical characteristic determines the class. Where two or more aggressive characteristics lead to the same class, the environment shall be classified into the next higher class, unless a special study for this specific case proves that it is not necessary.

Durability is then specified either through the traditional practice of limiting values of concrete composition (more widely used) or by performance-related methods. The requirements shall take into account the intended service life of the concrete structure.

Table 1.2.2 Limiting values for exposure classes for chemical attack from natural soil and ground water.

Chemical characteristic	Reference test method	XA1	XA2	XA3
Ground water				
SO_4^{2-} (mg/l)	EN 196-2	200 – 600	600 – 3000	3000 – 6000
pH	ISO 4316	5.5 – 6.5	4.5 – 5.5	4.0 – 4.5
CO_2 (mg/l)	prEN 13577	15 – 40	40 – 100	100 – saturation
NH_4^+ (mg/l)	ISO 7150	15 – 30	30 – 60	60 – 100
Mg^{2+} (mg/l)	ISO 7980	300 – 1000	1000 – 3000	3000 –saturation
Soil				
SO_4^{2-} tot(mg/kg)	EN 196-2	2000 – 3000	3000 – 12000	12000 – 24000
Acidity (ml/kg)	DIN 4030-2	> 200	Not encountered in practice	

1.2.1 Limiting values for concrete composition

In the absence of European standards for absolute performance testing of concrete, requirements for the method of specification to resist environmental actions are given in EN 206 in terms of established concrete properties and ***limiting values for concrete composition***. The requirements for each exposure class shall be specified in terms *of permitted types and classes of constituent materials, maximum water/cement ratio, minimum cement content, minimum concrete compressive strength class (optional), and if relevant minimum air-content of the concrete*.

Due to lack of experience on how the classification of the environmental actions on concrete reflect local differences in the same nominal exposure class, the specific values of these requirements for the applicable exposure classes are given in the provisions valid in the place of use. A *recommendation* for the choice of limiting values for concrete composition and properties is given in Annex F (informative) of the EN 206 and are presented in Table 1.2.3.

Table 1.2.3 Recommended limiting values for composition and properties of concrete.

	Exposure classes																	
	No risk of corro-sion or attack	Carbonation – induced corrosion				Chloride – induced corrosion by sea water			Chloride – induced corrosion by other than sea water			Freeze/thaw attack				Aggressive chemical environments		
	X0	**XC1**	**XC2**	**XC3**	**XC4**	**XS1**	**XS2**	**XS3**	**XD1**	**XD2**	**XD3**	**XF1**	**XF2**	**XF3**	**XF4**	**XA1**	**XA2**	**XA3**
Maximum water/cement ratio	---	0.65	0.60	0.55	0.50	0.50	0.45	0.45	0.55	0.55	0.45	0.55	0.55	0.50	0.45	0.55	0.50	0.45
Minimum strength class	C 12/15	C 20/25	C 25/30	C 30/37	C 30/37	C 30/37	C 35/45	C 35/45	C 30/37	C 30/37	C 35/45	C 30/37	C 25/30	C 30/37	C 30/37	C 30/37	C 30/37	C 35/45
Minimum cement cont. (kg/m^3)	---	260	280	280	300	300	320	340	300	300	320	300	300	320	340	300	320	360
Minimum air content (%)	---	---	---	---	---	---	---	---	---	---	---	---	4.0	4.0	4.0	---	---	---
Other requirements												Aggregate in accordance with prEN 12620 with sufficient freeze/thaw resistance					Sulphate-resisting cement	

This values are based on the assumption of an intended service life of the structure of 50 years, and refer to the use of cement type CEM I conforming EN 197. The minimum strength classes were derived from the relationship between water/cement ratio and the strength class of concrete made with cement of strength class 32.5.

The provisions valid in the place of use of the concrete ***should include requirements under the assumption of an indented service life of at least 50 years*** under the anticipated maintenance conditions. For shorter or longer service life, less onerous or more severe requirements may be necessary. In these cases or for specific concrete compositions or specific corrosion protection requirements for the concrete cover of the reinforcement, special considerations should be made by the specifier for a specific site or by national provisions in general.

If the concrete is in conformity with the limiting values, *the concrete in the structure shall be deemed to satisfy the durability requirements* for the intended use in the specific environmental condition, *provided:*

- ✓ the concrete is properly placed, compacted and cured e.g. in accordance with ENV 13670 or other relevant standards;
- ✓ the concrete has the minimum cover to reinforcement in accordance with the relevant design standard required for the specific environmental condition, e.g. ENV 1992;
- ✓ the appropriate class was selected;
- ✓ the anticipated maintenance is applied.

1.2.2 Performance-related design methods

The requirements related to exposure classes may be established by using ***performance-related methods for durability*** and may be specified in terms of performance-related parameters, e.g., scaling of concrete in a freeze/thaw test. Guidance on the use of an alternative performance-related design method with respect to durability is given in Annex J (informative) of EN 206. The application of an alternative method depends on the provisions valid in the place of use of the concrete.

The performance-related method considers each relevant deterioration mechanism, the service life of the element or structure, and the criteria which define the end of this service life, in a quantitative way. *Such a method may be based on satisfactory experience with local practices in local environments, on data from an established performance test method for the relevant mechanism, or on* ***the use of proven predictive models.***

A *general guidance and some applications* are given:

- Some aggressive actions are best dealt with a *prescriptive approach*, e.g., alkali-silica reaction, sulphate attack, or abrasion.
- Performance-related design methods are more relevant to corrosion resistance and possibly, freeze-thaw resistance of concrete. This approach may be appropriate where:
  - a service life significantly differing from 50 years is required;
  - the structure is “special” requiring a lower probability failure;
  - the environmental actions are particularly aggressive, or are well defined;
  - standards of workmanship are expected to be high;
  - a management and maintenance strategy is to be introduced, perhaps with planned upgrading;
  - significant populations or similar structures, or elements, are to be built;
  - new or different constituent materials are to be used;
  - method based on limiting values for concrete composition has been used in design, but there has been a failure to conform.
- In practice, the level of durability achieved depends on a combination of design, materials, and execution.
- The sensitivity of the design concept, the structural system, the shape of members and structural/ architectural detailing are all significant design parameters for all methods of durability design.
- Compatibility of materials, the construction method, the quality of workmanship, levels of control and quality assurance are significant parameters for all methods of durability design.
- The required durability performance depends on the required service life, on the possible future use of the structure, on the particular protective measures, on the planned maintenance in service, and on the consequences of failure, in the particular local environment.

- For any required level of performance, it is possible to derive alternative equivalent solutions from different combinations of design, material and construction factors.
- The level of knowledge of the ambient and local micro-climate is important in establishing the reliability of performance-related design methods.

The performance-related methods that may be used include:

- The ***refinement of the method of limiting values for concrete composition***, based on *long-term experience* of local materials and practices, and on detailed knowledge of the local environment.
- ***Methods based on approved and proven tests*** that are representative of actual conditions and have approved performance criteria.
- ***Methods based on analytical models*** that have been calibrated against test data representative of actual conditions in practice.

The concrete composition and the constituent materials should be closely defined to enable the level of performance to be maintained. In applying the methods listed above, it is important to define in advance, at least the following:

- ✓ type of structure and its form,
- ✓ local environmental conditions,
- ✓ level of execution, and
- ✓ required service life.

Some assumptions and judgements on these issues will usually be necessary to reduce the chosen method to a pragmatic and practical level.

The orientation of the present work *is towards the development of performance-related methods based on analytical models that have been calibrated against test data representative of actual conditions in practice.*

1.3 Theoretical approach of deterioration rate

As observed in Fig. 1.1.2, all physical and mechanical mechanisms for concrete deterioration, except direct loading and imposed deformations, may exhibit their effect on concrete performance during the first year of the concrete service life (concrete at early-ages). The *chemical and biological mechanisms* actually start from the early beginning; however, their detrimental results are observed after the first year (concrete at late-ages).

In the majority of concrete structures steel reinforcement is used. *In reinforced concrete, the most serious deterioration mechanisms are those leading to* ***corrosion of the reinforcement,*** *which occurs after depassivation due to carbon dioxide or chloride ion penetration* [1,5,9,10]. Almost all other deterioration mechanisms can be controlled since the mix design and cast [1]. For example:

- against frost action: air-entraining materials should be used,
- in the case of alkali-aggregate reaction: the reactivity of aggregates should be initially examined,
- to prevent sulphate attack: sulphate resistant cement and low water-to-cement ratio should be used, etc.

Therefore, at least in this work, the modeling efforts will be focused mostly on the ***corrosion initiation mechanisms***. However, special characteristics, where other deterioration mechanisms depend on, will also be presented ***(acid, sulphate, alkali attack)***. Actually, these are also the main deterioration actions considered in EN 206 (corrosion of reinforcement induced either by carbonation or chlorides and chemical attack). Thus:

✓ After the definition of ***mix design and structure characteristics***,
✓ as well as an assumption regarding the ***environmental conditions*** where the structure will be found,
✓ and based on ***fundamental mathematical models*** that simulate the deterioration mechanisms and rate,
➢ the ***structure service life*** *can be reliably predicted.*

1.4 Structure of the present work

The main scope of this work is to present the methods based on analytical models that may be used for the concrete service life prediction, in compliance with the proposed performance-related design methods of European Standard EN 206.

In this framework, the structure of the present work is visualized in Fig. 1.4.1, presenting the *sequence and the interrelations between the main chapters.* Later, this same logical diagram will be followed in the software program development.

First, the essential parameters that characterize a ***concrete composition (mix design)*** are presented, and this is the main source on which all other concrete characteristics depend. In this chapter also, the mix design strategy to ensure a required service life to a specific concrete composition is presented. Second, the ***main chemical and volumetric characteristics*** of concrete are calculated (chemical composition of hydrated cementitious materials, porosity and related characteristics) and this is also another source to receive information for the composite properties of concrete such as strength and durability. Based on the selected mix design and the calculated characteristics, a first approximation of the ***compressive strength class of concrete*** is presented.

Then each significant deterioration mechanism, according to the specific environment where the structure would be found, is presented and modeled. ***Concrete carbonation*** and ***chloride penetration*** are the most common causes for reinforcement corrosion and further concrete deterioration. The service life of the structure found in these environments that cause either carbonation or chloride attack is calculated. Other significant deterioration mechanisms are also presented (***chemical attack***).

Finally, ***cost and environmental aspects*** regarding concrete composition are full analysed. Now, for the initially selected concrete composition the most essential properties have been predicted, such as ***strength, service life and cost***. The *specifier* can then alter accordingly the concrete composition to improve further every desired property.

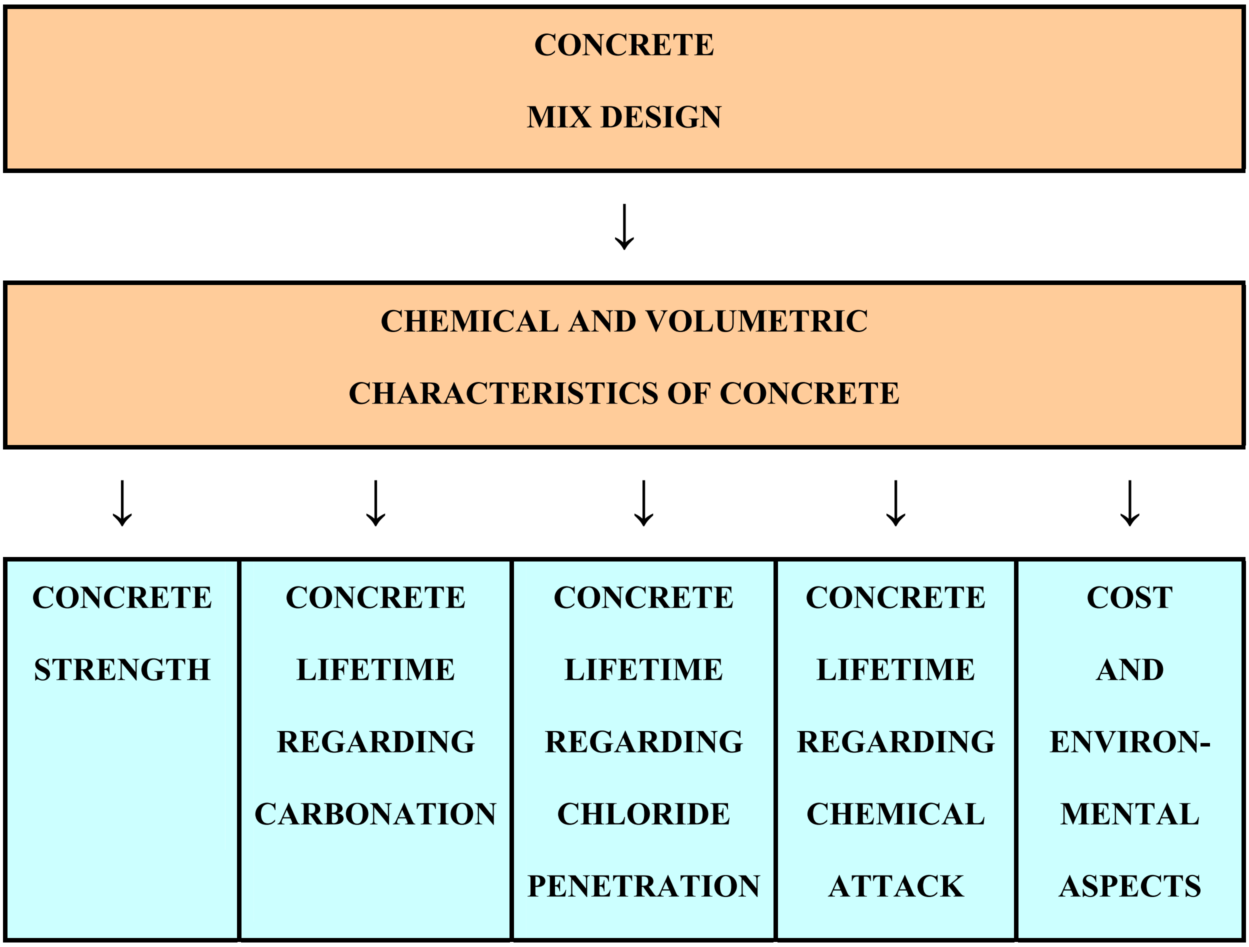

Figure 1.4.1 Structure of the present work presenting the sequence and the interrelations between the main chapters.