ESTIMATION OF
CONCRETE SERVICE LIFE
The Theoretical Background

by

Vagelis G. Papadakis

Chemical Engineer, PhD

Patras, Greece, 2005

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V.G. Papadakis & Associates
Building Technology & Durability
Patras Science Park S.A.
Stadiou Str., Platani, GR-26504, Patras, Greece
Tel.: +30 2610 911571 & +30 6932 327323
Fax: +30 2610 911570 e-mail: vgp@psp.org.gr

Foreword

Concrete is the most widely used building material. Despite of the significant advances made in concrete technology in recent years, the problems of unsatisfactory durability of structures are in a dramatic increase. Deterioration of concrete in service may be the result of a variety of mechanical, physical, chemical or biological processes. *Corrosion of steel reinforcement* is the most serious durability problem of reinforced concrete structures. It impairs not only the appearance of the structure, but also its strength and safety, due to the reduction in the cross-sectional area of the reinforcement and to the deterioration of bond with the surrounding concrete.

Over the past 50 years, an enormous amount of energy has been expended in laboratory and field studies on *concrete durability*. The results of this research are still either widely scattered in the journal literature or mentioned briefly in the standard textbooks. Moreover, the theoretical approaches of deterioration mechanisms with a predictive character are limited to some complicated mathematical models not widely applicable in practice. A significant step forward could be the development of appropriate *software for computer estimation*, including the reliable mathematical models and strengthened by adequate experimental data. Within this framework, the present work is the *theoretical background* where such software is based, as well as the *permanent reference* to explain any inquires and check further the reliability of the results.

In the present work, a *mix design strategy* to fulfil any requirements on strength and service life is presented. The *chemical and volumetric characteristics* of concrete are first estimated and the *service life of the concrete structure* is then predicted, based on fundamental models developed earlier mostly by the present author. The prediction is focused on the basic deterioration phenomena of the reinforced concrete, *carbonation and chloride penetration.* Aspects on *concrete strength* and *production cost* are also considered. The proposed models enable mixture proportions to be accurately specified and concrete performance reliably predicted. This work is the *source book* for the development of the software for estimation of concrete service life, EUCON$^{®}$. In general, this work concerns *Construction Engineers* and *Building Material Manufacturers* towards fundamental comprehension of materials behavior. Basic principles of Chemical Engineering are applied to simulate the physicochemical processes, yielding simple and accurate mathematical models for *design* and *prediction.* The work structure presented herein is in full compliance with the new *European Standards for cement: EN 197 and concrete: EN 206.*

The experimental research and mathematical modeling has been carried out by the present author as a part of various national and European Union research programs in Greece and Denmark, during the last 20 years. The *General Secretariat for Research and Technology, Ministry of Development, Greece,* provided financial support for the present work through the PRAXE Programme (02-PRAXE-86).

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Vagelis G. Papadakis
April 2005

Dr. *Vagelis G. Papadakis* holds a diploma in Chemical Engineering (1986) from the University of Patras, Greece, and a Ph.D. on the subject of carbonation and durability of concrete from the same institution (1990). He has a 20-year experience on scientific and demonstration projects on durability and technology of concrete, authored many papers and awarded by the American Concrete Institute (Wason Medal for Materials Research- 1993). He worked as a Researcher at the Danish Technological Institute, Building Technology Division, Concrete Centre (1997-1999) on supplementary cementing materials in concrete, holding an EU-fellowship (Marie Curie Grant). He was head of Concrete Technology Laboratory of TITAN Cement company S.A., Greece (1999-2000). At the present, he is head of "V.G. Papadakis & Associates – Building Technology and Durability" an innovative firm placed in "Patras Science Park S.A." and he is also teaching the courses of "Construction

Materials” and “Plant Design and Economics” in the University of Patras and University of Ioannina.

Contents

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].

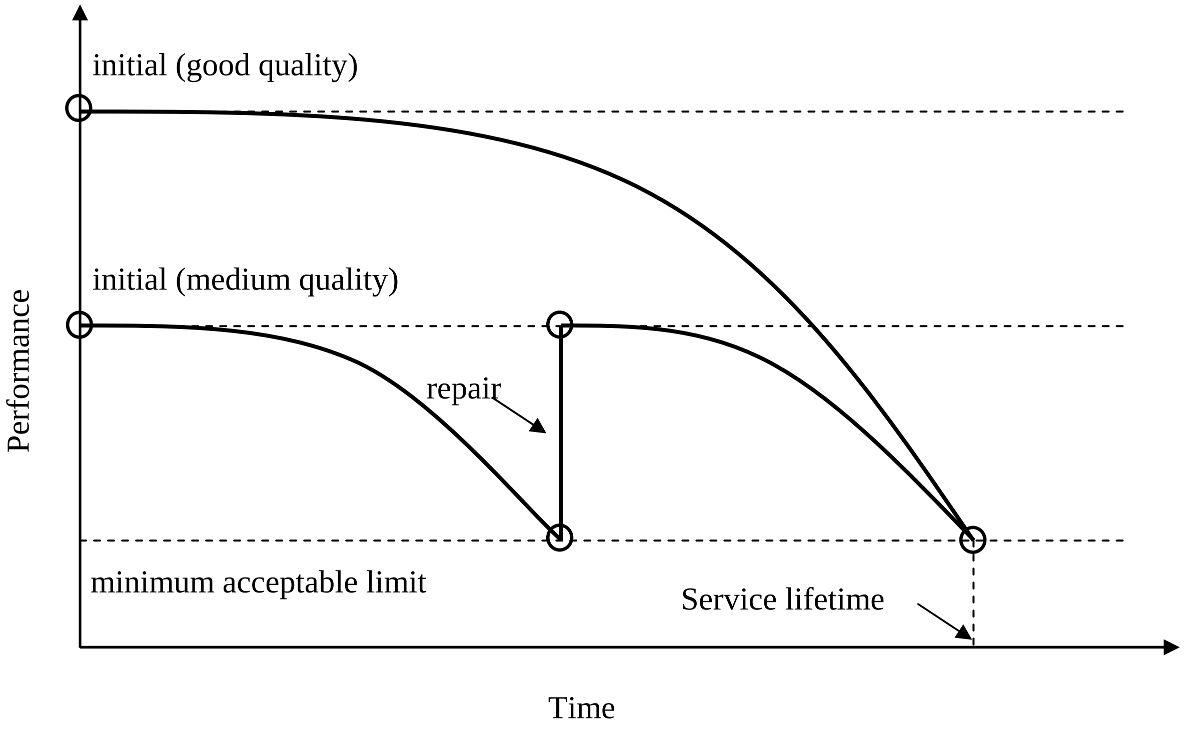

Figure 1.1.1 Relationship between concrete performance and service life.

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.

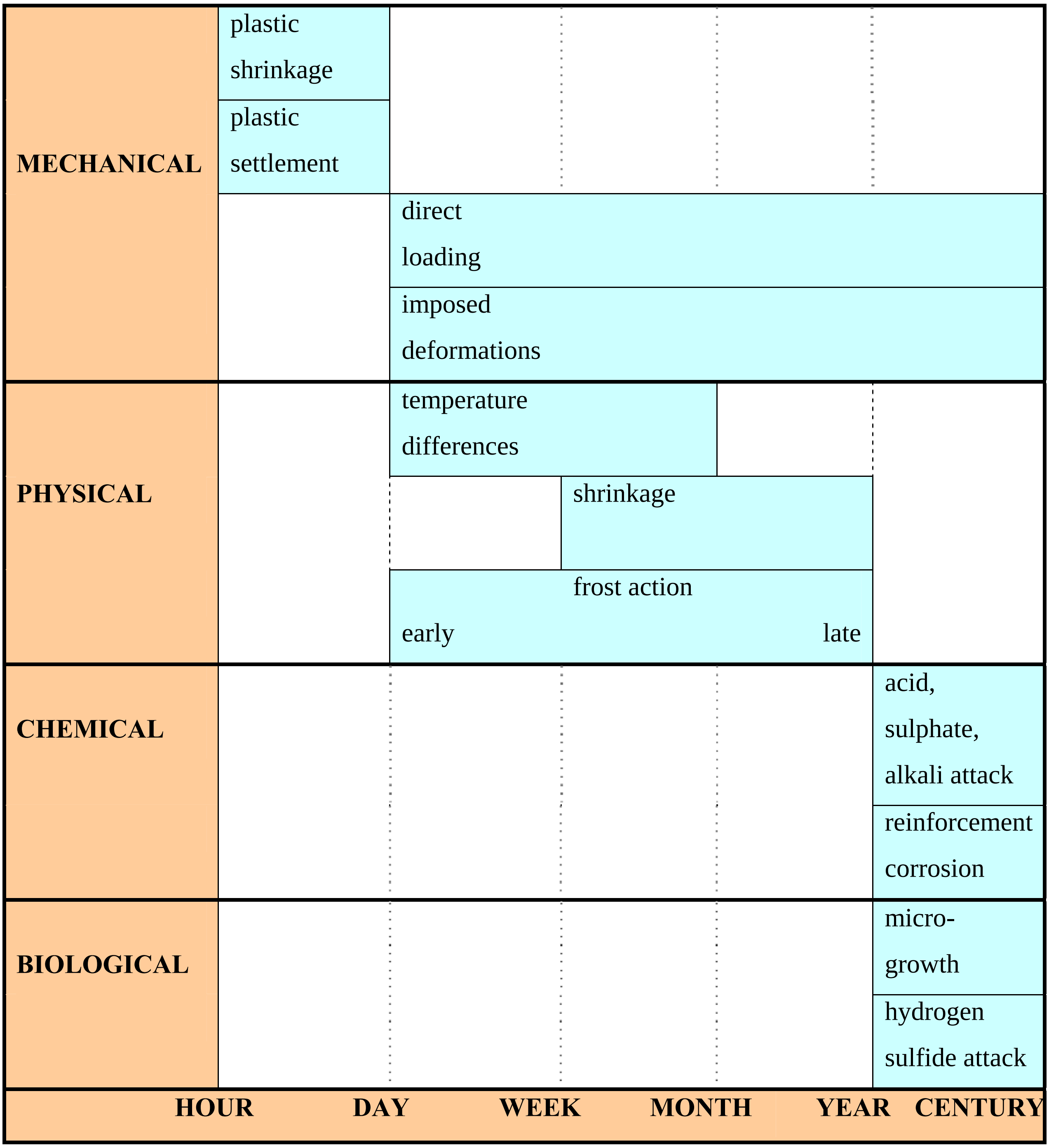

Figure 1.1.2 Deterioration mechanisms and most possible time of appearance of cracking.

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 corrosion 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.

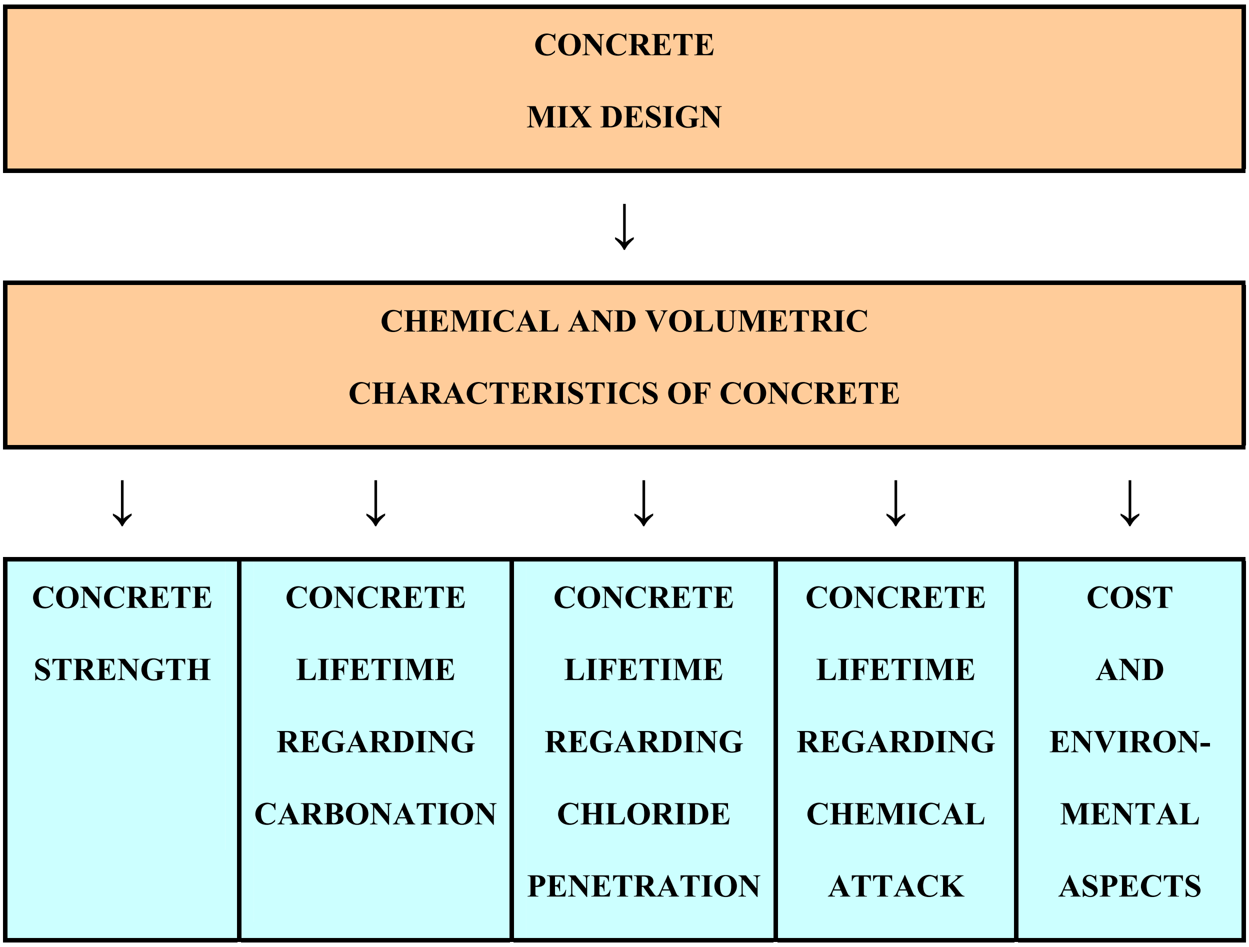

Figure 1.4.1 Structure of the present work presenting the sequence and the interrelations between the main chapters.

2. MIX DESIGN

2.1 Constituent materials for concrete composition

Concrete is the material formed by mixing cement, aggregates and water, with or without the incorporation of admixtures and additions, which develops its properties by hydration of the cement. The general concept for concrete mix design as presented herein is in full compliance with the most spread existing standards for concrete production, such as the *European Standard for concrete: EN 206* [12]. For the present application, a concrete volume is assumed that contains certain amounts of ***cement, additions (optional), aggregates, water, and admixtures (optional)*** *only*, see Fig. 2.1.1. To the above materials ***entrained or entrapped air*** should be added.

CONCRETE :

Cement: main constituents: portland clinker, blast furnace slag, silica fume, pozzolanic materials (natural or natural calcined pozzolanas), fly ash (siliceous or calcareous), burnt shale, and limestone
minor additional constituents: all main constituents except clinker
calcium sulphate, additives

\+

Additions: type I (filler aggregate, pigments), type II (fly ash, silica fume)

\+

Aggregates: fine, coarse

\+

Water: mixing water

\+

Admixtures: retarder, accelerator, air-entraining, plasticizer, superplasticizer, etc.

\+

Air: entrained, entrapped

Figure 2.1.1 Constituent materials for concrete composition.

All these materials have to comply with the corresponding standards for the constituent materials, for instance in the case of European Standards: EN 197 (Cement), EN 450 (Fly ash for concrete), EN 13263 (Silica fume for concrete), EN 12620 (Aggregates for concrete), EN 1008 (Mixing water for concrete), EN 934-2 (Admixtures for concrete), etc.

More specifically and for the purposes of the present application for the approach of concrete service life, we define as follows:

2.1.1 Cement

Cement is a hydraulic binder, i.e. a finely ground inorganic material which, when mixed with water, forms a paste that sets and hardens by means of hydration reactions and processes and which, after hardening, retains its strength and stability even under water. General suitability for concrete production is established for cement conforming to EN 197-1 [13]. Cement conforming to this European Standard, termed CEM cement, shall, when appropriately batched and mixed with aggregate and water, be capable of producing concrete or mortar which retains its workability for a sufficient time and shall after defined periods attain specified strength levels and also possesses long-term volume stability.

Hydraulic hardening of CEM cement is primarily due to the hydration of calcium silicates but other chemical compounds may also participate in the hardening process, e.g., aluminates. The sum of the proportions of reactive calcium oxide (CaO) and reactive silicon dioxide (SiO_2) in CEM cement shall be at least 50% by mass when proportions are determined in accordance with EN 196. CEM cements consist of different materials that are statistically homogeneous in composition resulting from quality assured production and material handling processes. According to this standard, a cement may comprise of ***main constituents, minor additional constituents, calcium sulphate and additives***, see Table 2.1.1.

A ***main constituent*** is a specially selected inorganic material in a proportion exceeding 5% by mass related to the sum of all main and minor additional constituents. As main constituents are used portland cement clinker, blast furnace slag, silica fume, pozzolanic materials (natural or natural calcined pozzolanas), fly ashes (siliceous or calcareous), burnt shale, and limestone.

Table 2.1.1 Types of common cements according to European Standard EN 197-1*.

Main types	Nota-tion	Main constituents**									Minor addit. const.
		K	S	D	P	Q	V	W	T	L/LL	
PORTLAND CEMENTS											
CEM I	I	95-100	-	-	-	-	-	-	-	-	0-5
PORTLAND-COMPOSITE CEMENTS											
CEM II	II/A-S	80-94	6-20	-	-	-	-	-	-	-	0-5
	II/B-S	65-79	21-35	-	-	-	-	-	-	-	0-5
	II/A-D	90-94	-	6-10	-	-	-	-	-	-	0-5
	II/A-P	80-94	-	-	6-20	-	-	-	-	-	0-5
	II/B-P	65-79	-	-	21-35	-	-	-	-	-	0-5
	II/A-Q	80-94	-	-	-	6-20	-	-	-	-	0-5
	II/B-Q	65-79	-	-	-	21-35	-	-	-	-	0-5
	II/A-V	80-94	-	-	-	-	6-20	-	-	-	0-5
	II/B-V	65-79	-	-	-	-	21-35	-	-	-	0-5
	II/A-W	80-94	-	-	-	-	-	6-20	-	-	0-5
	II/B-W	65-79	-	-	-	-	-	21-35	-	-	0-5
	II/A-T	80-94	-	-	-	-	-	-	6-20	-	0-5
	II/B-T	65-79	-	-	-	-	-	-	21-35	-	0-5
	II/A-L	80-94	-	-	-	-	-	-	-	6-20	0-5
	II/B-L	65-79	-	-	-	-	-	-	-	21-35	0-5
	II/A-M	80-94	6-20								0-5
	II/B-M	65-79	21-35								0-5
BLASTFURNACE CEMENTS											
CEM III	III/A	35-64	36-65	-	-	-	-	-	-	-	0-5
	III/B	20-34	66-80	-	-	-	-	-	-	-	0-5
	III/C	5-19	81-95	-	-	-	-	-	-	-	0-5
POZZOLANIC CEMENTS											
CEM IV	IV/A	65-89	-	11-35					-	-	0-5
	IV/B	45-64	-	36-55					-	-	0-5
COMPOSITE CEMENTS											
CEM V	V/A	40-64	18-30	-	18-30			-	-	-	0-5
	V/B	20-38	31-50	-	31-50			-	-	-	0-5

* The composition is expressed as % by mass of the main and minor additional constituents.

** Notation **exclusively** for the present table: portland clinker (K), blast furnace slag (S), silica fume (D), pozzolana (natural, P or natural calcined, Q), various fly ashes (siliceous, V or calcareous, W), burnt shale (T), and limestone (L or LL).

Portland cement clinker is the main constituent that all cement types contain (CEM I to CEM V). It is made by sintering a precisely specified mixture of raw materials (raw mill, paste or slurry) containing elements, usually expressed as oxides, CaO, SiO_2, Al_2O_3, Fe_2O_3 and small quantities of other materials. It is a hydraulic material which shall consist of at least 2/3 by mass of calcium silicates (3CaO. SiO_2 and 2CaO. SiO_2), the remainder consisting of aluminium and iron containing clinker phases and other compounds. The ratio by mass CaO/SiO_2 shall be not less than 2.0. The content of magnesium oxide (MgO) shall not exceed 5.0% by mass.

All other main constituents (except clinker), defined only in the present work as *supplementary cementing materials (SCM)*, may be divided into *natural materials* and *artificial* ones. To the former belong natural pozzolanic materials and limestone. To the second category belong granulated blast furnace slag, silica fume, calcined pozzolanas, fly ashes, and burnt shale. In EN 197 these materials defined as follows:

Granulated *blast furnace slag* is made by rapid cooling of a slag melt of suitable composition, as obtained by smelting iron ore in a blast furnace slag and contains at least 2/3 by mass of glassy slag and possesses hydraulic properties when suitably activated. It shall consist of at least 2/3 of the sum of ($CaO+MgO+SiO_2$), the remainder contains Al_2O_3 together with small amounts of other compounds. The ratio by mass of $(CaO+MgO)/(SiO_2)$ shall exceed 1.0.

Silica fume originates from the reduction of high purity quartz with coal in electric arc furnaces in the production of silicon or ferrosilicon alloys and consists of very fine spherical particles containing at least 85% by mass amorphous SiO_2.

In EN 197, *pozzolanic materials* are defined the *natural substances* of siliceous or silico-aluminous composition or a combination thereof (in general, however, pozzolanic materials are also fly ash and silica fume). Pozzolanic materials do not harden in themselves when mixed with water but, when finely ground and in the presence of water, they react at normal ambient temperature with dissolved calcium hydroxide, $Ca(OH)_2$, to form strength-developing calcium silicate and calcium aluminate compounds. These compounds are similar to those which are formed in the hardening of hydraulic materials. They consist essentially of reactive SiO_2 (>25.0 % by mass) and Al_2O_3, the remainder contains Fe_2O_3 and other oxides.

These materials may be *natural pozzolanas* (materials of volcanic origin or sedimentary rocks) or *natural calcined pozzolanas* (materials of volcanic origin, clays, shales or sedimentary rocks, activated by thermal treatment).

Fly ash is the combustion residue (coal mineral impurities) in coal-burning electric power plants, which flies out with the flue gas stream and is removed by electrostatic or mechanical precipitation. Ash obtained by other methods shall not be used in cement that conforms the EN 197-1. Fly ash may be siliceous or calcareous in nature. The former has pozzolanic properties; the latter may have, in addition, hydraulic properties. *Siliceous fly ash* is a fine powder of mostly spherical particles having pozzolanic properties. It consists essentially of reactive SiO_2 and Al_2O_3, the remainder contains Fe_2O_3 and other compounds. The proportion of reactive CaO shall be less than 10.0% by mass and the content of free CaO shall not exceed 1.0% by mass. The reactive SiO_2 content shall not be less than 25.0% by mass. *Calcareous fly ash* is a fine powder having hydraulic and/or pozzolanic properties. It consists essentially of reactive CaO, reactive SiO_2 and Al_2O_3, the remainder contains Fe_2O_3 and other compounds. The proportion of reactive CaO shall not be less than 10.0% by mass and the content of free CaO shall not exceed 1.0% by mass. The reactive SiO_2 content shall not be less than 25.0% by mass, if the reactive CaO is between 10-15% by mass; if the reactive CaO is greater than 15% by mass certain strength levels should be required.

Burnt shale, specifically burnt oil shale, is produced in a special kiln at temperatures of approximately 800 ^oC. Owing to the composition of the natural material and the production process, burnt shale contains clinker phases, mainly dicalcium silicate and monocalcium silicate. It also contains, besides small amounts of free calcium oxides and calcium sulphate, larger proportions of pozzolanically reacting oxides, especially SiO_2. Consequently, in a finely ground state burnt shale shows pronounced hydraulic properties like Portland cement and in addition pozzolanic properties.

Limestone shall meet the following requirements: The $CaCO_3$ content shall be at least 75% by mass, the clay content shall not exceed 1.20% by mass, and the total organic carbon content shall conform to one of the following criteria, LL: shall not exceed 0.20% by mass, L: shall not exceed 0.50% by mass

In general, but not accepted in EN 197, to the above SCM may be added slags from metallurgical furnaces producing steel, copper, nickel and lead, bottom ashes, ashes from incinerators and waste treatment sludge, metakaolin, red mud from alumina production, etc. These materials may, in some future revised edition of the standards, be included as cement constituents. However, either experimentally or at industrial scale all the the above additions are extensively used the recent years especially as ingredients in blended cements and at a lower degree as separately batched constituents in concrete [14-21]. *Almost only silica fume and siliceous fly ash are used as separately additions in concrete (see below: concrete additions).* However, all these materials, whatever is their origin in concrete, besides the effect on usual structural properties, such as strength and volume stability, *the concrete durability should seriously be considered.*

A ***minor additional constituent (mac)*** is a specially selected inorganic material used in a proportion not exceeding 5% by mass related to the sum of all main and minor additional constituents. As minor additional constituents can be used inorganic natural materials, inorganic mineral materials derived from the clinker production process or main constituents as specified earlier unless they are included as main constituents in the cement. Inert materials, such as limestone and dust derived from the clinker production process (materials known as fillers) are usually used. Thus, mac affect only the physical properties of concrete, such as workability and water retention. However, they shall not increase the water demand of the concrete appreciably, impair the resistance to deterioration or reduce the corrosion protection of the reinforcement.

Calcium sulphate (between 3 % and usually 5% by weight of cement) in the form of gypsum or anhydrite is added to the above constituents to control the clinker flash setting.

Various ***additives*** may also be added (up to 1% by weight of cement) to improve either the cement production or cement properties. They shall not promote the corrosion of the reinforcement or impair the properties of cement, mortar or concrete.

By studying Table 2.1.1, and of the purpose of understanding the various cements' behaviour, we can distinguish herein *five different categories of cement*, according to the SCM type that cement contains [16]:

1. **CEM I.** This is the type CEM I of cement, containing no additional SCM more than that in mac. An older name in the literature was ordinary Portland cement (OPC).
2. **CEM II/D.** This is the type CEM II/A-D of cement, containing a highly pozzolanic material (silica fume) at 6-10 % in cement (minus calcium sulphate).
3. **CEM II/ V,P,Q,M.** This covers the cement types CEM II/A-V, CEM II/B-V, CEM II/A-P, CEM II/B-P, CEM II/A-Q, CEM II/B-Q, CEM II/A-M, CEM II/B-M of cement, containing a normal pozzolanic material ([16], siliceous fly ash and natural or artificial pozzolanic materials) at 6-20 % (A) or 21-35% (B) in cement (minus calcium sulphate). This cement category can also cover the **CEM IV** cement types, whereas mostly normal pozzolanic materials are contained at higher contents: 11-35% (A) and 36-55% (B). The **CEM V** cement type requires a more detailed composition information; however as a first approximation it may be covered by this cement category, when burnt furnace slag is calculated almost as Portland clinker and normal pozzolanic materials are contained at 18-30 % (A) or 31-50% (B) in cement.
4. **CEM II/W,S,T.** This covers the cement types CEM II/A-W, CEM II/B-W, CEM II/A-S, CEM II/B-S, CEM II/A-T, CEM II/B-T of cement, containing a pozzolanic material with latent hydraulic properties ([16], calcareous fly ash, blast furnace slag and burnt shale) at 6-20 % (A) or 21-35% (B) in cement (minus calcium sulphate). This cement category can also cover the **CEM III** cement types, whereas a cementitious-pozzolanic material (blast furnace slag) is contained at higher contents: 36-65% (A), 66-80% (B), and 81-95% (C).
5. **CEM II/L.** This covers the cement types CEM II/A-L (or LL) and CEM II/B-L (or LL) of cement, containing a mineral admixture of low reactivity (limestone, L or LL) at 6-20 % (A) or 21-35% (B) in cement (minus calcium sulphate).

The ***standard strength of a cement*** is the compressive strength determined in accordance with EN 196-1 at 28 days and shall conform to the requirements in Table 2.1.2. *Three classes of standard strength are included; class 32,5, class 42,5 and class 52,5.* The *early strength* of a cement is the compressive strength at either 2 days or 7 days. Two classes of early strength are induced for each class of standard strength, a class with *ordinary early strength (N),* and a class with *high early strength (R).*

Table 2.1.2 Mechanical and physical requirements for common cements according to European Standard EN 197-1.

Strength class	Compressive strength (MPa)				Initial setting time (min)	Soundness (expansion) (mm)
	Early strength		Standard strength			
	2 days	7 days	28 days			
32,5 N	-	≥ 16.0	≥ 32.5	≤ 52.5	≥ 75	≤ 10
32,5 R	≥ 10.0	-	≥ 32.5	≤ 52.5	≥ 75	≤ 10
42,5 N	≥ 10.0	-	≥ 42.5	≤ 62.5	≥ 60	≤ 10
42,5 R	≥ 20.0	-	≥ 42.5	≤ 62.5	≥ 60	≤ 10
52,5 N	≥ 20.0	-	≥ 52.5	-	≥ 45	≤ 10
52,5 R	≥ 30.0	-	≥ 52.5	-	≥ 45	≤ 10

The initial setting time and expansion of cement shall conform to the requirements in Table 2.1.2. In EN 197, chemical requirements for the cements have also been specified.

Regarding ***durability requirements*** it is stated that, in many applications, particularly in severe environmental conditions, the choice of cement has an influence on the durability of concrete, mortar and grouts, e.g., frost resistance, chemical resistance and protection of the reinforcement. The choice of cement, particularly as regards type and strength class for different applications and exposure classes shall follow the appropriate standards and/or regulations for concrete or mortar valid in the place of use.

CEM cements shall be identified by at least the notation of the *cement type* as specified in Table 2.1.1 and the figures 32,5, 42,5 or 52,5 indicating the *standard strength class*, see Table 2.1.2. In order to indicate the *early strength class* the letter N or the letter R shall be added, see Table 2.1.2. ***The cement shall be selected*** from those for which the suitability is established, taking into account the execution of the work, the end use of concrete, the curing conditions, the dimensions of the structure (the heat development), the environmental conditions and the potential reactivity of aggregate to the alkalis from the constituents.

In the present work, we suppose that the cement belongs to one of the **CEM types** presented in Table 2.1.1, with strength class and early strength class as presented in Table 2.1.2. The total cement content in concrete is denoted by **C (kg cement / m^3 of concrete)**. The particle density (EN 196) of cement is denoted by **d_C (kg/m^3)**.

We also denote as **p_K (%)** the percentage of clinker (including the various additives) in the cement (minus calcium sulphate), **p_{CS} (%)** the percentage of calcium sulphate in the cement, **p_{MAC} (%)** the percentage of minor additional constituents in the cement (minus calcium sulphate), and **p_{SCM} (%)** the percentage of SCM in the cement (minus calcium sulphate). Obviously, we have:

$$[(p_K/100) + (p_{MAC}/100) + (p_{SCM}/100)]\, C\, (100-p_{CS})/100 + (p_{CS}/100)\, C = C \qquad (2.1.1)$$

Using Eq. (2.1.1) we can calculate p_{SCM} content when all other cement composition parameters are known:

$$p_{SCM} = 100 - p_K - p_{MAC} \qquad (2.1.2)$$

In the case of cement type CEM V, these composite cements contain, apart the clinker, certain amounts of both slag and other pozzolanic materials. The p_{SCM} (%) percentage of the total SCM in the cement (minus calcium sulphate) is separated in **p_{SL} (%)**, referring to slag percentage in cement, and **$p_{PO} = (p_{SCM} - p_{SL})$**, referring to the other pozzolanic materials.

2.1.2 Additions

Addition is a finely divided material used in concrete in order to improve certain properties or to achieve special properties. The EN 206 deals with two types of inorganic additions:

- *nearly inert additions* ***(type I)***
- *pozzolanic or latent hydraulic additions* ***(type II)***

General suitability as type I addition is established for *filler aggregate* conforming to EN 12620 and *pigments* conforming to EN 12878. General suitability as type II addition is established for ***fly ash*** conforming to EN 450 and ***silica fume*** conforming to EN 13263. However, EN 206 notes that certain constituents no conforming to some European Standard may be used in concrete; the establishment of suitability may result from: a European Technical Approval, or a relevant national standard or provisions. In general, type II additions may by all the above called supplementary cementing materials (SCM).

Type I additions may be calculated in the aggregate content. In the present work, we suppose that only fly ash and/or silica fume may be used as separate additions of type II in concrete. The fly ash content in concrete is denoted by **F (kg fly ash / m^3 of concrete)**. There is the possibility to use a specific **fly ash type**: siliceous (SIL) or calcareous (CAL). The silica fume content in concrete is denoted by **S (kg silica fume / m^3 of concrete)**. The particle densities of fly ash and silica fume are denoted as **d_F (kg/m^3)** and **d_S (kg/m^3)**, respectively.

We suppose also that *when these type II additions are used directly in concrete, a cement type CEM I is used as cement.* If however an other cement type is used we have to separate the pure portland clinker from all the other main constituents of cement. This portland clinker with the gypsum and mac is further considered as the only real cement; see further, portland cement in chapter 3. The other main constituents (SCM) have to be added, if they are active, to the above SCM content or, if they are inert, to the aggregates content.

2.1.3 Aggregates

Aggregate is a granular mineral material suitable for use in concrete. Aggregates may be natural (natural collected or just natural, and natural crushed), artificial or recycled from material previously used in construction. General suitability is established for:

- *normal and heavy-weight aggregates* conforming to EN 12620. Normal-weight aggregate has an oven-dry particle density between 2000 – 3000 kg/m^3, when determined according to EN 1097-6. Heavy-weight aggregate has an oven-dry particle density $\geq$ 3000 kg/m^3, when determined according to EN 1097-6.

- *light-weight aggregates* conforming to EN 13055-1. Light-weight aggregate of mineral origin has an oven-dry particle density ≤ 2000 kg/m^3 when determined according to EN 1097-6 or a loose oven-dry bulk density ≤ 1200 kg/m^3 when determined according to EN 1097-3.

Aggregate type, grading and categories, e.g., flakiness, freeze/thaw resistance, abrasion resistance, fines, ***shall be selected*** taking into account the execution of the work, the end use of the concrete, the environmental conditions and any requirements for exposed aggregate. The *maximum nominal upper aggregate size* (D_{max}) shall be selected taking into account the concrete cover to reinforcement and the minimum section width. When aggregates contain varieties of silica susceptible to attack by alkalies (Na_2O and K_2O originating from cement or other sources) and the concrete is exposed to humid conditions, actions shall be taken to prevent deleterious alkali – silica reaction using procedures of established suitability.

In the present work, the total aggregate content in concrete is denoted by **A (kg aggregate / m^3 of concrete)**. The particle density of aggregates is denoted as **d_A (kg/m^3)**. Aggregate/cement ratio (**A/C**) is the ratio of the aggregate content to cement content by mass in the fresh concrete.

2.1.4 Water

Suitability is established for ***mixing water*** and for recycled water from concrete production conforming to EN 1008. *Total water content* is the added water plus water already contained in the aggregates and on the surface of aggregates plus water in the admixtures and in additions used in the form of a slurry and water resulting from any added ice or steam heating. *Effective water content* is the difference between total water present in the fresh concrete and the water absorbed by the aggregates.

In the present work this ***effective water*** content is denoted by **W (kg water / m^3 of concrete)**. The water density is denoted as **d_W (kg/m^3)**. Water/cement ratio (**W/C**) is the ratio of the effective water content to cement content by mass in the fresh concrete.

2.1.5 Admixtures

Admixture is a material (usually organic) added during the mixing process of concrete in small quantities related to the mass of cement to modify the properties of fresh or hardened concrete. General suitability is established for admixtures conforming to EN 934-2.

In general, the admixtures for concrete can be divided into:

- admixtures modifying set and hardening:
    - accelerators
    - retarders
- admixtures modifying the mix rheology and the air content:
    - water-reducing admixtures (superplasticizers, plasticizers)
    - water-retaining admixtures
    - thickening admixtures
- admixtures entraining air into the mixes:
    - air-entraining and air-detraining admixtures
    - gas-forming admixtures
    - foam-forming admixtures
- admixtures modifying the resistance to physical and chemical actions:
    - frost-resisting and anti-freezing admixtures
    - water-repelling admixtures
    - permeability-reducing admixtures
    - corrosion-inhibiting admixtures
    - improving resistance to chemical actions

However, the most largely used products are *retarders* (0.2-0.4% by mass of cement), *accelerators* (0.5-6% by mass of cement), *air-entraining admixtures* (0.05-0.2% by mass of cement), *plasticizers* (0.3-0.5% by mass of cementitious materials), and *superplasticizers* (0.8-1.5% by mass of cementitious materials). These representative dosages refer to the total solution of admixtures (as supplied: solids plus solvent water).

The total amount of admixtures, if any, shall not exceed the *maximum dosage* recommended by the admixture producer and not exceed 50 g of admixture (as supplied) per kg cement unless the influence of the higher dosage on the performance and durability is established. If the total quantity of liquid admixtures exceeds 3 l/m^3 of concrete, its water content shall be taken into account when calculating the water/cement ratio.

In the present work, we suppose that one or more admixtures may be used, and the total admixture content in concrete is denoted by **D (kg of admixture solids / m^3 of concrete)**. The solids' density of admixtures is denoted by **d_D (kg/m^3)**. There is the possibility to use a specific **admixture type** (retarder, accelerator, air-entraining, plasticizer, superplasticizer, etc.) or a combination of them.

2.1.6 Entrained or entrapped air

Entrained air are the microscopic air bubbles intentionally incorporated in concrete during mixing, usually by use of a surface active agent; typically between 10 – 300 µm in diameter and spherical or nearly so. ***Entrapped air*** are voids in concrete which are not purposely entrained.

The total entrained and entrapped air content of concrete, when compacted in accordance with the procedure given in EN 12350-6, is denoted by **ε_{air} (m^3 of entrained or entrapped air / m^3 of concrete)**. It mainly depends on maximum aggregate size and the air-entraining agents' content. It shall be measured in accordance with EN 12350-7.

2.2 Basic calculations

As the **basis** for concrete composition, the volume unit of **1 m^3** of the fresh concrete is selected. By assuming negligible expansion this volume unit represents also hardened concrete. It must be emphasized that if *a material is added* to this unit, *then an equal volume of another component must be removed* in order to keep the same total volume and a common comparison basis. The composition of 1 m^3 of fresh concrete is given in Table 2.2.1. The following mass balance equation has to be fulfilled:

$$C/d_C + S/d_S + F/d_F + A/d_A + W/d_W + D/d_D + \varepsilon_{air} = 1 \tag{2.2.1}$$

This Eq. (2.2.1) may be used to calculate the *aggregate content* if all other composition parameters are known:

$$A = (1 - C/d_C - S/d_S - F/d_F - W/d_W - D/d_D - \varepsilon_{air})\, d_A \tag{2.2.2}$$

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 concrete. The *aggregate to cement ratio (A/C)* is calculated as the ratio of the aggregate content to cement content by mass in the fresh concrete. The *fresh concrete density*, d_{CON} (kg/m^3), is given by:

$$d_{CON} = C + S + F + A + W + D \tag{2.2.3}$$

Table 2.2.1 Composition of 1 m^3 volume of concrete.

C:	kg cement / m^3 of concrete	d_C:	cement density (kg/m^3)
S:	kg silica fume / m^3 of concrete	d_S:	silica fume density (kg/m^3)
F:	kg fly ash / m^3 of concrete	d_F:	fly ash density (kg/m^3)
A:	kg aggregates / m^3 of concrete	d_A:	aggregate density (kg/m^3)
W:	kg effective water / m^3 of concrete	d_W:	water density (kg/m^3)
D:	kg admixtures (solid) / m^3 of concrete	d_D:	admixture density (kg/m^3)
ε_{air}:	m^3 of entrained and/or entrapped air / m^3 of concrete		

2.3 Design strategy

The *concrete mixture composition* and the *constituent materials* for designed or prescribed concrete shall be chosen to satisfy the requirements specified for fresh and hardened concrete, including consistence, density, strength, durability, protection of embedded steel against corrosion, taking into account the production process and the intended method of execution of concrete works [12]. As *designed concrete* called the concrete for which the required properties and additional characteristics are specified to the producer who is responsible for providing a concrete conforming to the required properties and additional characteristics. As *prescribed concrete* called the concrete for which the composition and the constituent materials to be used are specified to the producer who is responsible for providing a concrete with the specified composition. Where not detailed in the specification, the producer shall select types and classes of constituent materials from those with established suitability for the specified environmental conditions.

In all specifications regarding concrete production, among the main design parameters are the *cement content (C)* and the *water-to-cement ratio (W/C).* Thus, minimum values of cement content and maximum values of W/C ratio are specified according to the *aggressiveness class* of the surrounding environment. Despite the exposure classes, in all cases, the *total equivalent cement content* should be taken into account [12].

After having specified the *fresh concrete composition (mix design: C, S, F W, A, D, and* ε_{air}*)* that fulfils the strength expectations and standard requirements (e.g., minimum C, maximum W/C ratio, etc.), the *concrete durability* should be examined. *Let us suppose that the* ***designed service life is Z years***. Thus, this specific concrete composition must be examined if it ensures service life greater than the designed one, as regards the possible deterioration environment in which the concrete will be exposed.

First the case of **concrete carbonation**, if any, must be taken into account. The ***concrete cover, c,*** must be higher than the expected carbonation depth within the lifetime Z. An accurate prediction of this carbonation depth can be obtained using the equations presented in section 5. If an *unacceptable* (due to various technical or economic reasons) cover is predicted then either a different concrete composition (e.g., lower W/C ratio, higher cement content, etc.) or a protective coating application shall be proposed. Then the calculation must be repeated until satisfaction.

Having specified the concrete composition and cover as above, the case of **chloride penetration**, if any, must then be considered. The equations presented in section 6 have to be solved using the corresponding parameters, in order to predict the chloride profile into the concrete as a function of time. Using the Cl-profile at the time equal to Z, the *minimum concrete cover* can be found at which and onwards the chloride concentration takes lower values than the *critical threshold* for corrosion. If an unacceptable cover is predicted then again either a denser concrete composition or a coating application should be considered and the calculations are repeated.

If any other deterioration mechanism could take place, e.g., a specific **chemical attack** (section 7), it has to be considered in a similar way. Finally, the ***cost of concrete production*** has to be estimated.

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 and/or the protection measures to improve further every desired property.

- The design parameters that ensure *full protection* (the higher concrete cover and the denser concrete composition or the best protection measures) among them predicted for resistance against carbonation and chloride penetration, chemical attack, etc., at the lowest cost, *must be finally proposed*.

3. PHYSICOCHEMICAL CHARACTERISTICS

3.1 Review of cementitious and pozzolanic reactions

3.1.1 Portland clinker hydration

Portland clinker consists essentially of crystalline compounds of calcium combined with silica, alumina, iron oxides, and sulphates. Typically, the approximate composition (including calcium sulphate) and amounts of the principal minerals present are: C_3S: 50%, C_2S: 25%, C_3A: 10%, C_4AF: 8% and gypsum $C\overline{S}H_2$: 5% (the notation of cement technology is used- *see Notation*).

Although the chemical reactions of *hydration of portland clinker compounds* are complex and do not proceed to completion, a *simplistic view* of the chemistry of the principal setting and hardening reactions may be presented in terms of chemical reactions. As regard the *hydration reactions of C_3S and C_2S*, many authors have agreed upon the following scheme [9,11,22-27]:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad (3.1.1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad (3.1.2)$$

It must be emphasized that the formula given for $C_3S_2H_3$ (C-S-H, calcium silicate hydrate) is only a very rough approximation, since not only is a material actually non-stoichiometric and very poorly crystalline, but also more than one variety of C-S-H is formed during hydration.

For the hydration of the other phases, C_3A and C_4AF, there is a vague image in the literature. In the case of *C_3A hydration*, Bensted [22] and Frigione [23] presented a satisfactory reaction scheme. In a system *without lime and gypsum* the reaction is the following:

$$2C_3A + 21H \rightarrow C_2AH_8 + C_4AH_{13} \rightarrow 2C_3AH_6 + 9H \qquad (3.1.3)$$

However, when lime is present (in the absence of gypsum), the C_3A hydration is described by:

$$C_3A + CH + 12H \rightarrow C_4AH_{13} \qquad (3.1.4)$$

This reaction is the principal cause of *flash set* in portland clinker, and in order to prevent it, gypsum is added to the clinker. When both lime and gypsum ($C\bar{S}H_2$) are present, as in the real case of cement hydration, in addition to Eq. (3.1.4) the following reactions take place:

$$C_4AH_{13} + 3C\bar{S}H_2 + 14H \rightarrow C_3A.3C\bar{S}.H_{32} + CH \qquad (3.1.5)$$

$$C_3A.3C\bar{S}.H_{32} + 2C_4AH_{13} \rightarrow 3C_4A\bar{S}H_{12} + 2CH + 20H \qquad (3.1.6)$$

As observed, C_3A begins its rapid reaction with lime and water to form calcium aluminate hydrate (C_4AH_{13}). There *immediately* follows a reaction between calcium sulphate in solution and the calcium aluminate hydrate to form ettringite ($C_3A.3C\bar{S}.H_{32}$, an insoluble compound that is deposited on the surface of the hydrating C_3A, providing an effective barrier against further rapid hydration). However, in a very short time ettringite reacts with calcium aluminate hydrate to form the more stable phase of monosulphate ($C_4A\bar{S}H_{12}$). When all the gypsum is used up, C_4AH_{13} continues to be formed from any remaining unhydrated C_3A and the final product is a monosulphate-C_4AH_{13} solid solution. If there is excess of gypsum then the main product is the monosulphate. By adding the Eq. (3.1.4)-(3.1.6), the overall equation of monosulphate formation is obtained:

$$\boxed{C_3A + C\bar{S}H_2 + 10H \rightarrow C_4A\bar{S}H_{12} \qquad (3.1.7)}$$

C_4AF, actually a solid solution within the C_2A-C_2F system, reacts at a slower rate than C_3A and forms iron (III) analogs of ettringite, monosulphate and calcium aluminate hydrate. However, when such reactions are used for calculations, an overestimation of water-bound content is observed. Therefore, a reaction that binds less water should take place. According to Frigione [23], gypsum (SO_4^{2-} ions) reacts preferentially with C_3A rather than C_4AF. In this case, practically in the absence of gypsum, the C_4AF hydration may be described by the following equation [27]:

$$C_4AF + 2CH + 10H \rightarrow C_6AFH_{12} \qquad (3.1.8)$$

The main product of clinker hydration is the *calcium silicate hydrate (C-S-H or CSH),* which is highly cementitious and constitutes about 60-65% of the total solids in a fully hydrated portland clinker. *Calcium hydroxide (CH)* is the second product of hydration (about 20%). It contributes little to the cementitious properties of the system, but offers the alkaline environment for the steel passivation. The remaining hydration products (about 15-20%) consist of calcium monosulphate aluminate hydrate and its iron analog, and calcium aluminate hydrate and its iron analog, and are capable of contributing strength to hardened cement paste.

3.1.2 Pozzolanic reactions

Supplementary cementing materials (SCM) are composed of the same oxides as portland clinker, but in different proportions and mineralogical compositions. As defined earlier, the reaction of these materials with $Ca(OH)_2$ (lime) is called *pozzolanic reaction*. Not all siliceous and aluminous materials are pozzolanic. It is known that crystalline minerals, e.g., silica as quartz, alumina as corundum, and aluminosilicates such as sillimanite (S.A) and mullite (3S.2A) *do not react* with lime solution at room temperature. *It is only when the siliceous and aluminous materials are present in non-crystalline (amorphous, glass) form and as fine particles, which they can hydrate at a slow rate in alkaline solutions*. This is *contrary to the hydration conditions in portland clinker* where the principal compounds are essentially crystalline, but decompose rapidly in water to provide the desired ions for formation of the cementitious hydrates. Therefore, it should be emphasized that the *mineralogical composition (glass phase content) and particle size* rather than the chemical composition would determine whether or not, or how fast a material can react with lime.

Particular attention should then be paid to *the nature of the possible reactants* in the pozzolans, and especially to glass content and type. As mentioned above, the crystalline materials are not active. An exception to this is high-calcium fly ash containing crystalline materials, such as C_3A and $C_4A_3\overline{S}$, which are reactive. Typically, fly ash contains 60-90% glass, granulated slags contain 85-95% glass, and condensed silica fume consists essentially of vitrified silica (almost 100% glass). The characteristics of the glassy phase in siliceous by-products, which range from simple (silica fume) to highly complex (fly ash) are reviewed elsewhere [15,28]. The “pozzolanic activity” is not limited to the lime-silica interaction, but includes all pozzolanic and cementitious reactions in the system: $CaO\text{-}SiO_2\text{-}Al_2O_3\text{-}Fe_2O_3\text{-}SO_3\text{-}H_2O$. It is accepted [14,17,29], that the difference between the “pozzolanic reactions” and portland clinker hydration reactions lies mainly in the reactants and the reaction rates, and not in the character of the hydration products. The *relative rates* of hydration of SCM depend, in general, on particle size and the composition of the non-crystalline phase. The reason for the slow reactivity is the mechanism of hydration according to which the particles hydrate essentially in situ by diffusion-controlled reactions. This is why particle size or surface area plays a dominant role in determining the relative rates of reactivity.

Knowing the reactants and the final products, and ignoring the intermediate steps, Papadakis et al. [30] were the first to propose a simplified scheme describing pozzolanic activity in terms of chemical reactions, but without an experimental verification. Later, Papadakis [31-34] developed a more reliable scheme for pozzolanic reactions with extended experimental verification. According to that analysis, the most plausible simplified equations, which can describe the pozzolanic activity of a *complex SCM* (containing active silica, amumina and calcium), are summarized as follows:

$$2S + 3CH \rightarrow C_3S_2H_3 \tag{3.1.9}$$

$$A + C\overline{S}H_2 + 3CH + 7H \rightarrow C_4A\overline{S}H_{12} \tag{3.1.10}$$

$$A + 4CH + 9H \rightarrow C_4AH_{13} \tag{3.1.11}$$

$$C_3A + C\overline{S}H_2 + 10H \rightarrow C_4A\overline{S}H_{12} \tag{3.1.12}$$

$$C + H \rightarrow CH \tag{3.1.13}$$

All this scheme describes sufficiently the cases when the SCM is *calcareous fly ash, blast furnace slag or similar SCM*. In the case when the SCM is *silica fume*, the Eq. (3.1.9) is the only valid. In the case when the SCM is *siliceous fly ash*, the Eqs. (3.1.9)-(3.1.11) are almost the only valid. The reaction (3.1.10), which dominates in high-gypsum systems, takes place *through several intermediate steps* including reaction (3.1.11), ettringite formation and its conversion to monosulphate.

3.2 Quantification of final products and pore volume

The portland clinker and the SCM can be easily analyzed in terms of oxides: total CaO (C), free CaO (Cf), SiO_2 (S), Al_2O_3 (A), Fe_2O_3 (F), SO_3 ($\overline{S}$), and other oxides, filler, or impurities denoted all by R. Let us denote then as $\mathbf{f_{i,K}}$ and $\mathbf{f_{i,P}}$ *the weight fractions of the constituent i* (i=C, Cf, S, A, F, $\overline{S}$, R) in the portland clinker and SCM, respectively. We assume that *mac* is almost filler without a significant participation in the chemical reactions. We denote herein as *"portland cement"* the sum of portland clinker, additives, and calcium sulphate, i.e., everything but cement's SCM and mac.

As mentioned in the previous sections not all of the total mass of the oxide i in an SCM is active (only the glass phase; with the exception of high-Ca SCM where some crystalline phases are also active). Let us denote by $\boldsymbol{\gamma_{i,P}}$ the weight fraction of the oxide i in the SCM, which contributes to the pozzolanic reactions (*"activity" ratio*).

Taking into account the cement composition presented in section 2, the clinker content in concrete, **K** (kg/m^3 of concrete), the cement's SCM content in concrete, **P** (kg/m^3 of concrete), the mac content in concrete, **MAC** (kg/m^3 of concrete), and the calcium sulphate content in concrete, **CS** (kg/m^3 of concrete), are given respectively by:

$$K = (p_K/100)\ C\ (100-p_{CS})/100 \qquad (3.2.1)$$

$$P = (p_{SCM}/100)\ C\ (100-p_{CS})/100 \qquad (3.2.2)$$

$$MAC = (p_{MAC}/100)\ C\ (100-p_{CS})/100 \qquad (3.2.3)$$

$$CS = (p_{CS}/100)\ C \qquad (3.2.4)$$

From the point of view of reinforcement protection, as well as for the completion of the pozzolanic activity, the quantity of calcium hydroxide, $Ca(OH)_2$, plays a dominant role (see carbonation chapter). The quantity of calcium-silicate-hydrate, $C_3S_2H_3$, is the main strength-bearing component in the hydrated cement (see strength chapter). The chemically-bound water, H, defines the minimum required water content for complete hydration of the cementitious materials. The concrete porosity, i.e., the ratio of total void volume to total concrete volume, plays a significant role in the propagation of the deterioration phenomena

[9-11]. In the sequence, and according to cement and addition type used, we distinguish the following separate cases for examination.

3.2.1 Cement type CEM I

a. Cement type CEM I without concrete additions

The weight fractions of the various phases (C_3S, C_2S, C_3A, C_4AF, $C\bar{S}H_2$) in portland clinker can be determined from the oxide analysis using Bogue's formulas [26,35]:

$$C_3S = 4.071(f_{C,K} - f_{Cf,K} - 0.7f_{\bar{S},K}) - (7.60f_{S,K} + 6.72f_{A,K} + 1.43f_{F,K}) \qquad (3.2.5)$$

$$C_2S = 2.867f_{S,K} - 0.754\,(C_3S) \qquad (3.2.6)$$

$$C_3A = 2.65f_{A,K} - 1.692f_{F,K} \qquad (3.2.7)$$

$$C_4AF = 3.043f_{F,K} \qquad (3.2.8)$$

The *portland clinker hydration reactions in presence of calcium sulphate (gypsum)* have been presented in section 3.1.1, and with an excess of gypsum, Eq. (3.1.1), (3.1.2), (3.1.7) and (3.1.8) are dominant. This is valid when $C\bar{S}H_2 > 0.637C_3A$; as applies typically when p_{CS} is about 5%. Using the stoichiometry of these reactions and the molar weights of the reactants and products (given in Table 3.2.1*), the amounts of the finally produced compounds* can be estimated. The Eq. (3.2.5)-(3.2.8) can be used to express these amounts as a function of the oxide contents in clinker. Thus, the amounts of CH, $C_3S_2H_3$ (CSH), $C_4A\bar{S}H_{12}$ ($CA\bar{S}H$), C_6AFH_{12} (CAFH), and chemically bound water (H) are given as follows, in kg/m^3 of concrete [11,31]:

$$CH = \{1.321(f_{C,K} - 0.7f_{\bar{S},K}) - (1.851f_{S,K} + 2.182f_{A,K} + 1.392f_{F,K})\}\,K \qquad (3.2.9)$$

$$CSH = 2.85f_{S,K}\,K \qquad (3.2.10)$$

$$CA\bar{S}H = (6.106f_{A,K} - 3.898f_{F,K})\,K \qquad (3.2.11)$$

$$CAFH = 5.099f_{F,K}\,K \qquad (3.2.12)$$

$$H = \{0.321(f_{C,K} - 0.7f_{\bar{S},K}) + 1.236f_{A,K} - 0.113f_{F,K}\}K \qquad (3.2.13)$$

Table 3.2.1 Molar weights and volumes of the main compounds found in portland cement and portland cement-based binders*

Compound	Molar weight x10^3 (kg/gmol)	Density x 10^{-3} (kg/m^3)	Molar volume x10^6 (m^3/gmol)
C_3S	228.30	3.20	71.34
C_2S	172.22	3.30	52.19
C_3A	270.18	3.03	89.17
C_4AF	485.96	3.77	128.90
$C\bar{S}H_2$	172.17	2.32	74.21
H	18.02	1.00	18.02
CH	74.10	2.24	33.08
$C_3S_2H_3$	342.41	≈ 2.28	≈ 150
$C_4A\bar{S}H_{12}$	622.51	1.95	319.24
C_4AH_{13}	560.47	2.06	272.07
$C_3A.3C\bar{S}.H_{32}$	1255.13	1.78	705.13
C_6AFH_{12}	814.31	2.65	307.87
$C_8AF\bar{S}_2H_{24}$	1302.44	≈ 2.3	≈ 560
C_8AFH_{26}	1178.29	≈ 2.3	≈ 500
$C\bar{C}$	100.09	2.71	36.93
C	56.08	3.32	16.89
S	60.08	2.20	27.28
A	101.96	4.00	25.49
F	159.69	5.24	30.48
$\bar{S}$	80.07	-	-

*Values taken from refs. [26,36-38]

In the above equations, free CaO was assumed to be completely converted to CH, whereas the remaining oxides (MgO, Na_2O, K_2O) was assumed not to participate in the reactions.

The *concrete porosity, ε,* defined as the ratio of pore volume to the total volume of concrete, is given by [11]:

$$\boxed{\varepsilon = \varepsilon_0 - \Delta\varepsilon_h - \Delta\varepsilon_P - \Delta\varepsilon_c \qquad (3.2.14)}$$

where ε_0 is the *porosity of fresh concrete*, and $\Delta\varepsilon_h$, $\Delta\varepsilon_p$, $\Delta\varepsilon_c$ are the *porosity reductions* due to hydration of portland clinker, pozzolanic activity, and carbonation, respectively. The initial value of porosity ε_0 is given by the expression:

$$\varepsilon_0 = \varepsilon_{air} + W/d_w \qquad (3.2.15)$$

where ε_{air} is the volume fraction of entrapped or entrained air in concrete (m^3/m^3), W the initial water content in concrete (kg/m^3) and d_w the water density (≈1000 kg/m^3). The reduction terms in Eq. (3.2.14) are due to the fact that the molar volume of the solid products of hydration, pozzolanic and carbonation reactions exceed that of the solid reactants.

For portland clinker concrete the term $\Delta\varepsilon_p$ equals zero. The term $\Delta\varepsilon_h$ is calculated by the following equation:

$$\Delta\varepsilon_h = \{(C_3S)\Delta\overline{V}_{C3S} + (C_2S)\Delta\overline{V}_{C2S} + (C_3A)\Delta\overline{V}_{C3A} + (C_4AF)\Delta\overline{V}_{C4AF}\}\ K \qquad (3.2.16)$$

where, $\Delta\overline{V}_j$ (j= C_3S, C_2S, C_3A, C_4AF) are the differences in molar volumes between solid products and solid reactants in hydration reactions, in m^3/kg. They can be calculated knowing the stoichiometry of the reactions and the molar volumes of the solid reactants and products (given in Table 3.2.1). For example, in the case of C_3S:

$$\Delta\overline{V}_{C3S} = (3/2 \text{ x } 33.08\text{x}10^{-6} + 1/2 \text{ x } 150 \text{ x } 10^{-6} - 71.34\text{x}10^{-6}) / (228.30\text{x}10^{-3})$$
$$= 0.2334\text{x}10^{-3}\ m^3/kg\ C_3S$$

Similarly, $\Delta\overline{V}_{C2S}$=0.2285x10^{-3} m^3/kg C_2S, $\Delta\overline{V}_{C3A}$=0.5769x10^{-3} m^3/kg C_3A, and $\Delta\overline{V}_{C4AF}$= 0.2321x$10^{-3}$ m^3/kg C_aAF. By substituting these values and the Eq.(3.2.5)-(3.2.8) in the Eq. (3.2.16), the *final value of the concrete porosity* can be obtained by the expression:

$$\varepsilon = \varepsilon_{air} + W/d_w - \\ -\{0.249(f_{C,K} - 0.7f_{\overline{S},K}) + 0.191f_{S,K} + 1.118f_{A,K} - 0.357f_{F,K})\}\ (K/1000) \qquad (3.2.17)$$

The reduction term due to the *complete concrete carbonation* is given by:

$$\Delta\varepsilon_c = (CH)\Delta\overline{V}_{CH} + (CSH)\Delta\overline{V}_{CSH} \qquad (3.2.18)$$

where $\Delta\overline{V}_{CH}$ (=0.05196x10^{-3} m^3/kgCH), and $\Delta\overline{V}_{CSH}$ (=0.04495x10^{-3} m^3/kg CSH), the differences in molar volumes between solid products and reactants in carbonation reaction of CH and CSH, respectively. Knowing the CH and CSH contents, the porosity reduction due to carbonation can be determined using Eq. (3.2.18) for all types of concrete.

b. Cement type CEM I with concrete additions: silica fume and/or fly ash

In this case we suppose that we have a type CEM I cement and may have also as concrete's additions: silica fume and/or fly ash (either siliceous or calcareous). When silica fume is added, the weight fraction of S in silica fume, $f_{S,S}$, and its active part, $\gamma_{S,S}$, are relevant to the quantitative calculations. When a siliceous fly ash is added, the weight fractions of S and A in fly ash, $f_{S,F}$ and $f_{A,F}$, and their active part, $\gamma_{S,F}$ and $\gamma_{A,F}$, are relevant to the quantitative calculations. In addition when the fly ash is calcareous, the weight fractions of C and $\overline{S}$ in fly ash, $f_{C,F}$ and $f_{\overline{S},F}$, are also used.

When additions are used in concrete, in addition to portland clinker hydration reactions, the pozzolanic reactions (3.1.9)-(3.1.13) take place. We assume that, the sulphate content, both from cement and additions, is higher than that required for the full hydration of the clinker and the completion of the pozzolanic reactions. Taking into account the stoichiometry of these reactions, after complete evolution of the hydration and pozzolanic action, the following *"final"* contents are calculated [31-34]:

$$
\begin{aligned}
\mathbf{CH} &= \{\, 1.321\,(f_{C,K} - 0.7\, f_{\bar{S},K}) - (1.851\, f_{S,K} + 2.182\, f_{A,K} + 1.392\, f_{F,K})\,\}\, K \\
&\quad - 1.851\, \gamma_{S,S}\, f_{S,S}\, S \\
&\quad - \{\, (1.851\, \gamma_{S,F}\, f_{S,F} + 2.182\, \gamma_{A,F}\, f_{A,F}) - 1.321\,(f_{C,F} - 0.7 f_{\bar{S},F})\,\}\, F && (3.2.19) \\
\mathbf{CSH} &= 2.85\,(f_{S,K}\, K + \gamma_{S,S}\, f_{S,S}\, S + \gamma_{S,F}\, f_{S,F}\, F) && (3.2.20) \\
\mathrm{CA\bar{S}H} &= (6.106\, f_{A,K} - 3.898\, f_{F,K})\, K + 6.106\, \gamma_{A,F}\, f_{A,F}\, F && (3.2.21) \\
\mathrm{CAFH} &= 5.099\, f_{F,K}\, K && (3.2.22) \\
\mathbf{H} &= \{\, 0.321\,(f_{C,K} - 0.7\, f_{\bar{S},K}) + 1.236\, f_{A,K} - 0.113\, f_{F,K}\,\}\, K \\
&\quad + \{0.321\,(f_{C,F} - 0.7\, f_{\bar{S},F}) + 1.236\, \gamma_{A,F}\, f_{A,F}\,\}\, F && (3.2.23)
\end{aligned}
$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{min} > H$. Similarly, the minimum water to cement ratio $(W/C)_{min}$ is defined as H/C.

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.19) must be positive (i.e., $CH \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of silica fume and fly ash. Writing again Eq. (3.2.19) as:

$$
\mathrm{CH} = q_K\, K - q_S\, S - q_F\, F \qquad (3.2.19a)
$$

where:

$$
\begin{aligned}
q_K &= \{\, 1.321\,(f_{C,K} - 0.7\, f_{\bar{S},K}) - (1.851\, f_{S,K} + 2.182\, f_{A,K} + 1.392\, f_{F,K})\,\} && (3.2.19b) \\
q_S &= \{\, 1.851\, \gamma_{S,S}\, f_{S,S}\,\} && (3.2.19c) \\
q_F &= \{\, (1.851\, \gamma_{S,F}\, f_{S,F} + 2.182\, \gamma_{A,F}\, f_{A,F}) - 1.321\,(f_{C,F} - 0.7\, f_{\bar{S},F})\,\} && (3.2.19d)
\end{aligned}
$$

we distinguish the below cases; determining simultaneously the *maximum part of silica fume that may participate in the pozzolanic reactions (defined as S_{ACT}) and the corresponding part for fly ash (defined as F_{ACT}):*

a. If only silica fume is added (F=0 and S≠0):

$S \leq (q_K / q_S)\, K$, then: $S_{ACT} = S$ (3.2.24a)

$S > (q_K / q_S)\, K$, then: $S_{ACT} = (q_K / q_S)\, K$ (3.2.24b)

In the latter case, the CH=0, and the rest of silica fume ($S\text{-}S_{ACT}$) is inert.

b. If only fly ash is added (S=0 and F≠0):

$F \leq (q_K / q_F)\, K$, then: $F_{ACT} = F$ (3.2.25a)

$F > (q_K / q_F)\, K$, then: $F_{ACT} = (q_K / q_F)\, K$ (3.2.25a)

In the latter case, the CH=0, and the rest of fly ash ($F\text{-}F_{ACT}$) is inert.

c. If both silica fume and fly ash are added (S≠0 and F≠0):

$q_S\, S + q_F\, F \leq q_K\, K$, then: $S_{ACT} = S$ and $F_{ACT} = F$ (3.2.26a)

$q_S\, S + q_F\, F > q_K\, K$ then: $S_{ACT} = S$ and $F_{ACT} = [(q_K / q_F)\, K - (q_S / q_F)\, S]$ (3.2.26b)

In the latter case, the CH=0, and if $S \leq (q_K / q_S)\, K$ (as usually valid – otherwise go to the case *a.,* with all fly ash inert), then the whole quantity of silica fume will react preferably with the produced CH from clinker hydration, and afterwards, part of fly ash will react with any remaining CH. Thus in the latter case only the $F_{ACT} = [(q_K / q_F)\, K - (q_S / q_F)\, S]$ of fly ash is active and the rest of fly ash ($F\text{-}F_{ACT}$) is inert.

Obviously, the active contents must be inserted in the Eq. (3.2.19)-(3.2.23), as well in the following determining porosity. In the case when active CaO is added, i.e., as lime putty, this is added to the CH content increasing thus the active parts of silica fume and/or fly ash [39-41].

The porosity reduction, because of the pozzolanic reaction ($\Delta\varepsilon_p$) of silica fume is negligible [32], and only the pozzolanic reaction of fly ash decreases porosity. If the gypsum content is higher than the maximum required, the term $\Delta\varepsilon_p$ is calculated as:

$$\Delta\varepsilon_p = (\gamma_A\, f_{A,F}\, F)\, \Delta\overline{V}_{A,\bar{S}} + (f_{C,F} - 0.7 f_{\bar{S},F})\, F\, \Delta\overline{V}_C \qquad (3.2.27)$$

where $\Delta\overline{V}_{A,\bar{S}}$ and $\Delta\overline{V}_C$ are the molar volume differences for the reactions (3.1.10) and (3.1.13) respectively (equal to $1.18\text{x}10^{-3}$ m^3/kg and $0.289\text{x}10^{-3}$ m^3/kg respectively). By substituting the $\Delta\varepsilon_h$ and $\Delta\varepsilon_p$ terms in Eq. (3.2.14), the *final* value of the porosity, ε, of a non-carbonated concrete (cement CEM I and using additions silica fume and/or fly ash), and ε_C of a totally carbonated concrete, are given by:

$$\begin{aligned}\varepsilon \; = \; & \varepsilon_{air} + W/d_w \\ & - \{\, 0.249\,(f_{C,K} - 0.7\, f_{\bar{S},K}) + 0.191\, f_{S,K} + 1.118\, f_{A,K} - 0.357\, f_{F,K} \,\}\,(K/1000) - \\ & - \{\, 0.289\,(f_{C,F} - 0.7\, f_{\bar{S},F}) + 1.18\, \gamma_{A,F}\, f_{A,F} \,\}\,(F/1000) \qquad (3.2.28)\end{aligned}$$

$$\varepsilon_C = \varepsilon - \{\, (CH)\, 0.05196\text{x}10^{-3} + (CSH)\, 0.04495\text{x}10^{-3} \,\} \qquad (3.2.29)$$

Typical values of $f_{i,K}$ and $f_{i,P}$, i.e., *the weight fractions of the constituent i* (i=C, S, A, F, $\bar{S}$) in the portland clinker and various SCM, respectively, are presented in Table 3.2.2. The oxide activity ratios also for each SCM, $\gamma_{i,P}$, is included (a mean value, both for silica and alumina).

Table 3.2.2 Typical oxide analysis (%) and activity ratios, γ (%), of portland clinker, silica fume, siliceous and calcareous fly ashes, and various SCM used in EN 197 [data from 31-34, 14-20].

	Cementitious/pozzolanic materials	**S**	**A**	**F**	**C**	**$\bar{S}$**	**γ**
1	Portland clinker	23	6	3	65	0.5	-
2	Blast furnace slag	36	9	1	40	0.5	90
3	Silica fume	91	1	1.5	0.7	0.4	96
4	Pozzolana (natural)	58	15	5	6	1	50
5	Pozzolana (natural, calcined)*	53	42	1	0.1	0	80
6	Siliceous fly ash	53	20	9	4	0.6	82
7	Calcareous fly ash	39	16	6	24	4.3	71
8	Burnt shale	38	10	6	35	5	90
9	Limestone	2	1	0.2	2	0.1	50
10	Various SCM for CEM II	50	16	7	12	1.5	65
11	Various SCM for CEM IV	50	20	7	10	1	65
12	Various SCM for CEM V	50	20	7	10	1	65

* Metakaolin

3.2.2 Cement types CEM II, CEM III, CEM IV

In this general case, we suppose that we have any of types CEM II, CEM III, or CEM IV of cement. No other extra SCM is added as a separate concrete addition. The cement's SCM content in concrete is denoted as P (kg/m^3 of concrete) and is given by Eq. (3.2.2). When SCM exists in cement, in addition to portland clinker hydration reactions, the pozzolanic reactions (3.1.9)-(3.1.13) take place. We assume that, the sulphate content, both from cement and SCM, is higher than that required for the full hydration of the clinker and the completion of the pozzolanic reactions. Taking into account the previous analysis, the following *"final"* contents and porosities are calculated:

$$\mathbf{CH} = \{\, 1.321\,(f_{C,K} - 0.7\, f_{\bar{S},K}) - (1.851\, f_{S,K} + 2.182\, f_{A,K} + 1.392\, f_{F,K}) \,\}\, K$$

$$- \{\, (1.851\, \gamma_{S,P}\, f_{S,P} + 2.182\, \gamma_{A,P}\, f_{A,P}) - 1.321\,(f_{C,P} - 0.7\, f_{\bar{S},P}) \,\}\, P \qquad (3.2.30)$$

$$\mathbf{CSH} = 2.85\,(f_{S,K}\, K + \gamma_{S,P}\, f_{S,P}\, P) \qquad (3.2.31)$$

$$CA\bar{S}H = (6.106\, f_{A,K} - 3.898\, f_{F,K})\, K + 6.106\, \gamma_{A,P}\, f_{A,P}\, P \qquad (3.2.32)$$

$$CAFH = 5.099\, f_{F,K}\, K \qquad (3.2.33)$$

$$\mathbf{H} = \{\, 0.321\,(f_{C,K} - 0.7\, f_{\bar{S},K}) + 1.236\, f_{A,K} - 0.113\, f_{F,K} \,\}\, K$$

$$+ \{\, 0.321\,(f_{C,P} - 0.7\, f_{\bar{S},P}) + 1.236\, \gamma_{A,P}\, f_{A,P} \,\}\, P \qquad (3.2.34)$$

$$\boldsymbol{\varepsilon} = \varepsilon_{air} + W/d_w$$

$$- \{\, 0.249\,(f_{C,K} - 0.7\, f_{\bar{S},K}) + 0.191\, f_{S,K} + 1.118\, f_{A,K} - 0.357\, f_{F,K} \,\}(K/1000)$$

$$- \{\, 0.289\,(f_{C,P} - 0.7\, f_{\bar{S},P}) + 1.18\, \gamma_{A,P}\, f_{A,P} \,\}\,(P/1000) \qquad (3.2.35)$$

$$\boldsymbol{\varepsilon_C} = \varepsilon - \{\, (CH)\, 0.05196\text{x}10^{-3} + (CSH)\, 0.04495\text{x}10^{-3} \,\} \qquad (3.2.36)$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{min} > H$.

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.30) must be positive ($CH \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of SCM. Writing again Eq. (3.2.30) as follows:

$$CH = q_K\, K - q_P\, P \qquad (3.2.30a)$$

where:

$$q_K = \{ 1.321 (f_{C,K} - 0.7 f_{\bar{S},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} \qquad (3.2.30b)$$

$$q_P = \{ (1.851 \gamma_{S,P} f_{S,P} + 2.182 \gamma_{A,P} f_{A,P}) - 1.321 (f_{C,P} - 0.7 f_{\bar{S},P}) \} \qquad (3.2.30c)$$

the following condition has always to be considered; determining the *maximum part of SCM that may participate in the pozzolanic reactions (defined as P_{ACT})*:

$$P \leq (q_K / q_P) K, \quad \text{then:} \quad P_{ACT} = P \qquad (3.2.37a)$$

$$P > (q_K / q_P) K, \quad \text{then:} \quad P_{ACT} = (q_K / q_P) K \qquad (3.2.37b)$$

In the latter case, the CH=0, and the rest of SCM: $(P-P_{ACT})$ is inert.

Obviously, the active contents must be inserted in the Eq. (3.2.30)-(3.2.36).

3.2.3 Cement type CEM V

In this case, we suppose that we have a type CEM V cement. No other extra SCM is added to the concrete mixture. This composite cement contains, apart the clinker, certain amounts of both slag and other pozzolanic materials. The p_{SCM} (%) percentage of the total SCM in the cement (minus calcium sulphate) is separated in $\mathbf{p_{SL}}$ **(%)**, referring to slag percentage in cement, and $\mathbf{p_{PO} = (p_{SCM} - p_{SL})}$, referring to the other pozzolanic materials. The cement's slag content in concrete, denoted by **SL** (kg/m^3 of concrete), and the cement's pozzolan content (except slag) in concrete, denoted by **P** (kg/m^3 of concrete), are given by:

$$SL = (p_{SL}/100)\, C\, (100-p_{CS})/100 \qquad (3.2.38)$$

$$P = [(p_{SCM} - p_{SL})/100]\, C\, (100-p_{CS})/100 \qquad (3.2.39)$$

Taking into account the previous analysis, the following *"final"* contents and porosities are then calculated:

$$\mathbf{CH} = \{ 1.321 (f_{C,K} - 0.7 f_{\bar{S},K}) - (1.851 f_{S,K} + 2.182 f_{A,K} + 1.392 f_{F,K}) \} K$$

$$\begin{aligned}
& && -\{(1.851\,\gamma_{S,SL}\,f_{S,SL} + 2.182\,\gamma_{A,SL}\,f_{A,SL}) - 1.321\,(f_{C,SL} - 0.7\,f_{\bar{S},SL})\}\,SL \\
& && -\{(1.851\,\gamma_{S,P}\,f_{S,P} + 2.182\,\gamma_{A,P}\,f_{A,P}) - 1.321\,(f_{C,P} - 0.7\,f_{\bar{S},P})\}\,P && (3.2.40) \\
& \mathbf{CSH} &=\ & 2.85\,(f_{S,K}\,K + \gamma_{S,SL}\,f_{S,SL}\,SL + \gamma_{S,P}\,f_{S,P}\,P) && (3.2.41) \\
& \mathbf{H} &=\ & \{0.321\,(f_{C,K} - 0.7\,f_{\bar{S},K}) + 1.236\,f_{A,K} - 0.113\,f_{F,K}\}\,K \\
& && +\{0.321\,(f_{C,SL} - 0.7\,f_{\bar{S},SL}) + 1.236\,\gamma_{A,SL}\,f_{A,SL}\}\,SL \\
& && +\{0.321\,(f_{C,P} - 0.7\,f_{\bar{S},P}) + 1.236\gamma_{A,P}\,f_{A,P}\}\,P && (3.2.42) \\
& \varepsilon &=\ & \varepsilon_{air} + W/d_w \\
& && -\{0.249\,(f_{C,K} - 0.7\,f_{\bar{S},K}) + 0.191\,f_{S,K} + 1.118\,f_{A,K} - 0.357\,f_{F,K}\}\,(K/1000) \\
& && -\{0.289\,(f_{C,SL} - 0.7\,f_{\bar{S},SL}) + 1.18\,\gamma_{A,SL}\,f_{A,SL}\}\,(SL/1000) \\
& && -\{0.289\,(f_{C,P} - 0.7\,f_{\bar{S},P}) + 1.18\,\gamma_{A,P}\,f_{A,P}\}\,(P/1000) && (3.2.43) \\
& \varepsilon_C &=\ & \varepsilon - \{(CH)\,0.05196\text{x}10^{-3} + (CSH)\,0.04495\text{x}10^{-3}\} && (3.2.44)
\end{aligned}$$

The minimum water content required for the completion of clinker hydration and pozzolanic reactions has to be $W_{min} > H$.

For the *completion of the pozzolanic activity*, the left-hand side of Eq. (3.2.40) must be positive ($CH \geq 0$). Otherwise, there will not be enough lime solution to react with the entire quantity of the pozzolanic constituents of slag and pozzolans. Rewriting Eq. (3.2.40) as follows:

$$CH = q_K\,K - q_{SL}\,SL - q_P\,P \qquad (3.2.40a)$$

where:

$$q_K = \{1.321\,(f_{C,K} - 0.7\,f_{\bar{S},K}) - (1.851\,f_{S,K} + 2.182\,f_{A,K} + 1.392\,f_{F,K})\} \qquad (3.2.40b)$$

$$q_{SL} = \{(1.851\,\gamma_{S,SL}\,f_{S,SL} + 2.182\,\gamma_{A,SL}\,f_{A,SL}) - 1.321\,(f_{C,SL} - 0.7\,f_{\bar{S},SL})\} \qquad (3.2.40c)$$

$$q_P = \{(1.851\,\gamma_{S,P}\,f_{S,P} + 2.182\,\gamma_{A,P}f_{A,P}) - 1.321\,(f_{C,P} - 0.7\,f_{\bar{S},P})\} \qquad (3.2.40d)$$

the following condition has always to be considered; determining the *maximum parts of slag and pozzolan that may participate in the pozzolanic reactions (defined respectively as* SL_{ACT} *and* P_{ACT}*):*

q_{SL} SL + q_P P $\leq$ q_K K, then: SL_{ACT} = SL and P_{ACT} = P (3.2.45a)

q_{SL} SL + q_P P > q_K K (3.2.45b)

In the latter case, the CH=0, and assuming that both slag and pozzolans react at the same rate with the produced CH, we calculate this similar degree of reaction, **r**, as follows:

$$r = (q_K K) / (q_{SL} SL + q_P P) \tag{3.2.46}$$

Then, only the (r SL) of slag is active (SL_{ACT}) and the rest [(1-r) SL] is inert. Similarly, only the (r P) of the pozzolanic materials is active (P_{ACT}) and the rest [(1-r) P] is inert.

3.3 Estimation of reaction kinetics

Expressions for the rates, $r_{h,i}$ ($mol/m^3.s$), of the *hydration reaction* of the portland clinker phases (i= C_3S, C_2S, C_3A, C_4AF) have been presented in a previous publication [11]. They were obtained from measurements [24,27] of the fraction $F_{h,i}$ (t) of compound i, which has been hydrated at time t (s) after mixing (*degree of hydration*), and have the form:

$$r_{h,i} \equiv -dC_i/dt = k_{h,i}\, C_i^{ni} / C_{i,0}^{ni-1} \tag{3.3.1}$$

$$F_{h,i} \equiv 1 - C_i / C_{i,0} = 1 - [1 - k_{h,i}\, t(1-n_i)]^{1/(1-ni)} \tag{3.3.2}$$

in which C_i and $C_{i,0}$ are the current and the initial (at t=0) molar concentrations of compound i, respectively (mol/m^3), $k_{h,i}$ and n_i kinetic parameters for the compound i depending on fineness, curing conditions and temperature. Fitted values of the exponents n_i and the coefficients $k_{h,i}$ (for curing temperature of 20 ^oC) are listed in Table 3.3.1. For another curing temperature, θ (^oC), the following relationship may be used [1]:

$$k_{h,i} = k_{h,i}(20\,^oC)\ \exp\left[(E/R)\,(1/293 - 1/(273+\theta)) \right] \tag{3.3.3a}$$

$$E = 33500 + 1470\,(20-\theta) \quad \text{for } \theta < 20^oC, \text{ and} \tag{3.3.3b}$$

$$E = 33500 \quad \text{for } \theta \geq 20\,^oC \tag{3.3.3c}$$

Table 3.3.1 Hydration parameters for major clinker components*.

	C_3S	C_2S	C_3A	C_4AF
Exponent n_i	2.65	3.10	2.41	3.81
Coefficient $k_{h,i}$ x 10^3, kg/gmol	1.17	0.16	2.46	1.00

*for CEM I 42.5N, 20 °C

where E is the mean activation energy for the hydration reactions (J/gmol) and R the gas universal constant (8.314 J/gmol.K)

Similar rate expressions can describe the *pozzolanic reactions*, Eq. (3.1.9)-(3.1.13). In this case, the pozzolanic activity is revealed after a certain period of time, denoted as t*, ("incubation period" of pozzolanic activity). This period is approximately 1 day for silica fume, 2 weeks for low-calcium fly ash and 3 days for high-calcium fly ash or blast furnace slag [14]. Thus, the reaction rate, $r_{p,j}$, of an active oxide j of the pozzolan (j=S,A,C) can be described as follows:

$$r_{p,j} = 0, \quad 0 \leq t \leq t^* \tag{3.3.4}$$

$$r_{p,j} \equiv -dC_j/dt = k_{p,j}\, C_{j,0}\, (1-F_{p,j})^{nj} = k_{p,j}\, C_j^{nj} / C_{j,0}^{nj-1}, \quad t^* \leq t \tag{3.3.5}$$

$$F_{p,j} \equiv 1 - C_j / C_{j,0} = 1 - [1-k_{p,j}\, t(1-n_j)]^{1/(1-nj)} \tag{3.3.6}$$

By fitting these expressions in experimental results of fraction $F_{p,j}$ of reacted oxide j as a function of time, the parameter values can be obtained. Usually, only CH-content and compressive strength results are available for the estimation of the degree of pozzolanic reaction. However, as was observed in H-content results [31], the presence of SCM in concrete *alters* the hydration rates of the clinker compounds. Therefore, the CH-content or the strength differences at an intermediate time cannot be attributed exclusively to pozzolanic reactions. For example, the C_3A and C_4AF hydration is significantly retarded in the presence of pozzolans. A complete kinetic analysis should include the hydration rate alterations of the portland clinker individual compounds. With the present results, such analysis is not possible.

Moreover, in such a case the final picture would be very complicated. Thus, the *development degree of the main concrete characteristics (CH-content, porosity, strength)* can be estimated better using the experimental results given in this or similar works, leaving the pure fundamental approach for a future work.

4. STRENGTH APPROXIMATION

4.1 The European Standard EN 206 and strength aspects

According to EN 206 [12], the hardened concrete *is classified* with respect to its *compressive strength* according to Table 4.1.1 (for normal-weight and heavy-weight concrete; for light-weight concrete, see [12]). The characteristic compressive strength at 28 days of 150 mm diameter by 300 mm cylinders ($f_{ck,cyl}$) or the characteristic strength at 28 days of 150 mm cubes ($f_{ck,cube}$) may be used for classification. *Characteristic strength* is the value of strength below which 5% of the population of all possible strength determinations of the volume of concrete under consideration, are expected to fall.

Table 4.1.1 Compressive strength classes for normal-weight and heavy-weight concrete.

Compressive strength class	Minimum characteristic cylinder strength ($f_{ck,cyl}$, MPa)	Minimum characteristic cube strength ($f_{ck,cube}$, MPa)
C8/10	8	10
C12/15	12	15
C16/20	16	20
C20/25	20	25
C25/30	25	30
C30/37	30	37
C35/45	35	45
C40/50	40	50
C45/55	45	55
C50/60	50	60
C55/67	55	67
C60/75	60	75
C70/85	70	85
C80/95	80	95
C90/105	90	105
C100/115	100	115

Where the strength is to be determined, it shall be based on tests carried out on either 150 mm cubes or 150/300 mm cylinders conforming to EN 12390-1 and made and cured in accordance with EN 12390-2 from samples taken in accordance with EN 12350-1.

When compressive strength is to be determined, it shall be expressed as $f_{c,cube}$ where determined using cubical specimens and $f_{c,cyl}$ where determined using cylindrical specimens, in accordance with EN 12390-3. Unless specified otherwise, the compressive strength is determined on specimens tested at 28 days. For particular uses, it may be necessary to specify the compressive strength at ages earlier or later than 28 days or after storage under special conditions. The characteristic strength of the concrete shall be equal or greater than the minimum characteristic compressive strength for the specified compressive strength class, see Table 4.1.1.

The producer shall provide the user the compressive strength class of the concrete and, if requested, information on the *strength development* of the concrete either in terms of Table 4.1.2 or by a strength development curve at 20 °C between 2 and 28 days. The *strength ratio* to indicate the strength development is the ratio of the mean compressive strength after 2 days ($f_{cm,2}$) to the mean compressive strength after 28 days ($f_{cm,28}$), determined from initial tests or based on known performance of concrete of comparable composition.

Table 4.1.2 Strength development of concrete at 20 °C.

Strength development	Estimate of strength ratio ($f_{cm,2} / f_{cm,28}$)
Rapid	≥ 0.5
Medium	≥ 0.3 to < 0.5
Slow	≥ 0.15 to < 0.3
Very slow	< 0.15

On the other hand, EN 206 gives a detailed system for *conformity control*, i.e., the combination of actions and decisions to be taken in accordance with conformity rules adopted in advance to check the conformity of the concrete with the specification. The conformity or non-conformity is judged against the conformity criteria.

The *conformity control for designed concrete* with respect to compressive strength has as follows. For normal-weight and heavy-weight concrete of strength classes from C8/10 to C55/67 sampling and testing shall be performed either on individual concrete compositions or on concrete families of established suitability. A *concrete family* is a group of concrete compositions for which a reliable relationship between relevant properties is established and documented. The family concept shall not be applied to concrete of higher strength classes. A distinction is made for *initial production* (until 35 at least results are available) and *continuous production* (when at least 35 test results are obtained over a period not exceeding 12 months). Sampling of concrete shall be randomly selected and taken in accordance with EN 12350-1.

The *conformity assessment for compressive strength* shall be made on test results taken during an assessment period that shall not exceed the last 12 months. Conformity is assessed on specimens tested at 28 days (or at another specified age) for:

- groups of "n" non-overlapping or overlapping consecutive test results f_{cm} *(criterion 1);*
- each individual test result f_{ci} *(criterion 2)*

Conformity is confirmed if both the criteria given in Table 4.1.3 for either initial or continuous production are satisfied. Where conformity is assessed on the basis of a concrete family, criterion 1 is to be applied to the reference concrete taking into account all transposed test results of the family; criterion 2 is to be applied to the original test results. To confirm that each individual member belongs to the family, the mean of all non-transposed test results (f_{cm}) for a single family member shall be assessed against a specific *criterion 3* [12]. Initially the *standard deviation* σ shall be calculated from at least 35 consecutive test results taken over a period exceeding the 3 last months.

Table 4.1.3 Conformity criteria for compressive strength.

Production	**Number “n” of test results in the group**	**Criterion 1** **Mean of “n” results (f_{cm}, MPa)**	**Criterion 2** **Any individual test result (f_{ci}, MPa)**
Initial	≥3	$\geq f_{ck} + 4$	$\geq f_{ck} - 4$
Continuous	≥15	$\geq f_{ck} + 1.48\ \sigma$	$\geq f_{ck} - 4$

4.2 Concrete strength approximation using cement’s strength class

For a CEM I type of cement, many researchers have shown that the main strength components in hydrated paste are C_3S and C_2S due to CSH production, see section 3 [9,22-27]. However, in the early stages of hydration (0-7 days) the alumino-ferrite phases, especially in the presence of gypsum, make a significant contribution to the total strength. At an advanced (>28 days) or “complete” hydration level, the strength that the C_3A or C_4AF phase (in the presence of gypsum) can contribute is only 10% of the strength of the C_3S or C_2S phase. As these phases (C_3A and C_4AF) are present at a low concentration in the cement, it is principally the product of C_3S and C_2S, *i.e. CSH,* that is correlated with the total strength of the hydrated cement. Another also strong parameter is the *concrete porosity*, especially in the *transition zone* between cement paste and aggregate surface. Thus, a strength prediction approach could be developed based on fundamental chemical and volumetric characteristics, as these given in the previous section 3, i.e., CSH content, porosity, etc.

However, a reliable prediction of concrete strength based on contribution of each individual compound is very difficult, because this contribution is not simply additive and has been found to depend on age and the curing conditions [9, 25]. Moreover, a generally applicable strength prediction equation is not possible due to interaction between the various compounds, including additions and cement’s SCM, the influence of alkalis and gypsum, the influence of the particle size of cement and the influence of particle size and shape of aggregates, etc. Many attempts have been made to generate strength prediction of cement paste, mortar and concrete, but without a generally accepted validity. On the other hand, many *empirical expressions* have been proposed for strength prediction, presenting the most crucial dependences of strength from concrete compositional parameters and calculating the adjustable parameters from experiments [9,25,26,36,42,43].

In all empirical expressions the W/C ratio turns out to be the most important parameter. Probably the first formulation of the relation of strength, (f_c, mean compressive strength, MPa) and the concrete constituents was made by Feret [43,44]:

$$f_c \;=\; b\,(C/d_C)^2 \,/\, (C/d_C + W/d_W + \varepsilon_{air})^2 \qquad (4.2.1a)$$

$$\text{or}\;\; f_c \;=\; b \,/\, [1 + (W/C)\,(d_C/d_W) + \varepsilon_{air}\,(d_C/C)]^2 \qquad (4.2.1b)$$

where b is a parameter adjustable from experimental results. Another famous relationship is that introduced by Abrams [43,44]:

$$f_c \;=\; b_1 \,/\, b_2^{W/C} \qquad (4.2.2)$$

where again b_1 and b_2 are adjustable parameters dependent on cement type, curing and age at test. Also another empirical equation is that deduced by Bolomey [31,45-47]:

$$f_c = p_1 \left(\frac{1}{W/C} - p_2\right) \qquad (4.2.3)$$

where p_1 is a *strength factor* depending on cement type, aggregate type and air content (MPa) and p_2 a *time factor* depending mainly on time, type of curing, and early strength class (cement fineness). All the above rules, as well many others more complicated, require experimental results for the parameter adjustment.

In the lack of experimental results the information from the ***cement strength class*** may be used to estimate a safe lower limit for concrete strength and thus to approach the corresponding value of ***compressive strength class***. European Standard EN 196-1 prescribes a compressive strength test for cement on mortar specimens of fixed composition. The specimens are tested as 40 mm equivalent cubes, and are made with a “CEN standard sand”, natural, siliceous, and rounded. The W/C ratio is 0.5 and the sand/cement ratio is 3. The specimens are cured in water at 20 °C until testing on 2 or 7, and 28 days. Through this approach the cement strength class is defined [13]. However, when strength results from mortars are compared with ones from concretes made each with the same W/C ratio, a significant difference is observed. The *concrete strength is higher than the mortar strength*, mostly due to greater amount of entrapped air in mortar [9]. Using for example all the above information to the Feret's formula (W/C=0.5, $d_C/d_W \approx 3.15$, $\varepsilon_{air} \approx 0.035$, $d_C \approx 3150$, $C \approx 490$), a lower value for parameter b can be estimated:

$$f_c = b / [1 + (W/C)(d_C/d_W) + \varepsilon_{air}(d_C/C)]^2 \geq SS \tag{4.2.4a}$$

$$\text{i.e.,}\ b \geq 7.84\ SS \tag{4.2.4b}$$

where *SS is the standard strength class (at 28 days) of cement (MPa)*. Using Eq. (4.2.4), *the minimum compressive strength class of concrete (at 28 days)* can be estimated at another values of W/C, C or ε_{air} from the following equation:

$$\boxed{f_c \geq 7.84\ SS / [1 + (W/C)(d_C/d_W) + \varepsilon_{air}(d_C/C)]^2} \tag{4.2.5}$$

If rounded aggregates are used for concrete the above estimation has to decrease by a factor of 13% [44]. On the other hand, if a strength result from the above mortar specimens is known at another age (2, 7, or 90 days), this could be used in Eq. (4.2.5), as SS, in order to estimate the compressive strength at the same age and for other W/C values. In this way, the *strength development* can be predicted.

Several other empirical expressions may be used as above, i.e., Abrams', Eq. (4.2.2) or Bolomey's, Eq. (4.2.3), etc. However, Feret's formula as contains only one adjustable parameter permits a rather safer approximation from the others models with more adjustable parameters. On the other hand, it contains the effect of air content (ε_{air}) predicting that 1% variation in air content results in a variation of about 4.5% of the compressive strength as many experimental results have shown [48]. As Feret's formula was extracted from mixes of rather high W/C, at modern lower W/C mixes another exponent (than 2.0) may be used in Eq. (4.2.1). In any case, this approach is just *a first rough approximation*, valuable for the initial test proportioning, and a detailed experimental verification is required. It has also to be emphasized that the above approach can be applied for any cement type, but it refers only to *concrete without any active additions such as fly ash or silica fume.* The next section is dealt with strength prediction when active additions are used.

4.3 Strength approximation using SCM efficiency factor

4.3.1 Procedure

When in a concrete, made with CEM I type of cement, a Type II addition is used (silica fume and/or fly ash), the Eq. (4.2.5) is not valid anymore, as it is. The pozzolanic action of addition shall be taken in consideration as it gives strength components. In the previous section 3, a simplified scheme describing the activity of supplementary cementing materials (SCM) in terms of chemical reactions was proposed, yielding quantitative expressions for the estimation of the final chemical and volumetric composition of such SCM-concretes. However, a practical approach to the effect of SCM on the strength of portland cement systems and on their resistance against carbonation and chloride penetration can be achieved, using the concept of the *SCM efficiency factor*. We assume that when active additions are used in concrete a cement of type CEM I is used only.

The *efficiency factor (or k-value)* is defined as the part of the SCM that can be considered as equivalent to portland cement (CEM I), providing the same concrete properties (*obviously k=1 for portland cement*). The quantity of the SCM in the concrete mixture can be multiplied by the k-value to estimate the *equivalent cement content*, which can be added to the cement content for the determination of the water-to-cement ratio, minimum required cement content, etc. The compressive strength was so far used as the property for the estimation of k-values [12,49]. In this work, durability properties are also used, such as resistance against carbonation and chloride penetration, and relative k-values are calculated [46,47,50,51]. Knowing these k-values, the mix design for preparation of the building product can be easier and more accurate.

In the case of SCM-concrete, the following expression for compressive strength can be used which involves the concept of k-value in Eq. (4.2.5):

$$f_c \geq 7.84\ SS / \{1 + [W/(C+k_F F_{ACT}+k_S S_{ACT})]\,(d_C/d_W) + \varepsilon_{air}\,[d_C/(C+k_F F_{ACT}+k_S S_{ACT})]\}^2 \qquad (4.3.1)$$

where F_{ACT} and S_{ACT} are the active contents of concrete additions fly ash and silica fume (kg/m^3), having an efficiency factor k_F and k_S respectively. These active contents are calculated in the previous section 3. Using this equation, and plenty of experimental results, the k-values for various SCM are calculated and summarized in Table 4.3.1.

For siliceous fly ashes, a k-value of 0.5 was calculated for 28 days' strength [31]. These very low calcium fly ashes are very common in the vast majority of EU, where similar k-values are proposed (0.3-0.5 [12,49,44]). However, as time proceeds, higher k-values are calculated for these fly ashes approaching those of high-calcium fly ashes (0.7 for 91 days and 1.1 for 1 year [31]). For calcareous fly ashes (as well for blast furnace slag [44] and burnt shale), the k-values are around unity (1) at early ages and they exceed it as time proceeds. This means that up to a certain level [33,34], these specific pulverized fly ashes can substitute, equivalently, for portland cement.

The natural SCM exhibit much lower efficiency factors (about 0.3-0.4 for natural pozzolana). This is correlated with their low level of active silica content.

In the case of an artificial pozzolan of low reactivity, very low k-values of 0-0.1 were calculated, proving that the lack of active silica due to slowly-cooled production plays a dominant role in pozzolanic activity. On the contrary, the metakaolin exhibits significant higher strengths, resulting at very high k-values (up to 3 at 28 days and onwards [51]). As this material was treated at high temperatures almost all silica was converted into amorphous and thus reactive. This behavior is similar to that of silica fume, where very high k-values were also calculated (3 at 28 days [31,44]).

Table 4.3.1 Efficiency factors (k-values) for various supplementary cementing materials [31,46,47,50,51]*.

Cementitious/ pozzolanic materials	Strength (2 days)	Strength (7 days)	Strength (28 days)	Strength (90 days)
Portland clinker	1	1	1	1
Silica fume	1	2	3	2.4
Pozzolana (natural)	0.4	0.3	0.3	0.3
Metakaolin	1	1.8	3	3
Siliceous fly ash	0.2	0.3	0.5	0.7
Calcareous fly ash	1.1	1.1	1.2	1

* All these SCM were ground prior to use up to a fineness of 400±20 m^2/kg according to Blaine's test.

According to EN 206, type II additions may be taken into account in the concrete composition with respect to the cement content and the W/C ratio if the suitability is established. The *suitability of the k-value concept* is established for siliceous fly ash and silica fume. If other concepts, e.g., the equivalent concrete performance concept, modifications on the rules of the k-value concept, higher k-values, other additions or combinations of additions are to be used, their suitability shall be established. The establishment of the suitability may result from either a European Technical Approach or a relevant national standard or provision valid in the place of use of concrete.

The EN 206 permits the k-value concept to be taken into account replacing the W/C ratio with W/(C+ k · addition) ratio and in the minimum cement content requirement. The actual value of k depends on the specific addition. EN 206, through EN 450, accepts only siliceous fly ash as type II addition in concrete. The maximum amount of siliceous fly ash to be taken into account for the k-value concept shall meet the requirement:

$$\text{Fly ash / cement} \leq 0.33 \text{ by mass} \qquad (4.3.2)$$

The following k-values are permitted for concrete containing cement type CEM I for siliceous fly ash addition:

CEM I 32.5 $k_F = 0.2$ (4.3.3a)

CEM I 42.5 and higher $k_F = 0.4$ (4.3.3a)

The maximum amount of silica fume to be taken into account for the k-value concept shall meet the requirement:

Silica fume / cement ≤ 0.11 by mass (4.3.2)

The following k-values are permitted for concrete containing cement type CEM I for silica fume addition:

for specified $W/C \leq 0.45$ $k_S = 2$ (4.3.3a)

for specified $W/C > 0.45$ $k_S = 2$ (except exp. classes XC and XF, where k=1) (4.3.3a)

In general, an agreement is observed between EN 206 recommendations and the present work's approach. For example, in the present work only the active parts of fly ash and silica fume are considered (typically for siliceous fly ash: $F_{ACT}=0.21C$, for calcareous fly ash: $F_{ACT}=0.48C$, and for silica fume: $S_{ACT}=0.14C$; when these materials are used alone). When both silica fume and fly ash used then lower active parts are estimated. On the other hand, for the case of siliceous fly ash and silica fume similar k-values are proposed by the EN 206.

The present work is more general from EN 206 giving the dependence of k-values on time, including the case of a combined use of both silica fume and fly ash and introducing also the use of calcareous fly ash as (a future) concrete addition. However, the EN 206 recommendations have to be applied officially without any alteration; the scope of the present work is just on strength prediction and thus it can be used for assistance on initial proportioning.

4.3.2 Experimental estimation of SCM efficiency factor

Pozzolanic activity is usually determined through an *activity index;* the ratio of the compressive strength of a pozzolanic mortar to that of a control mortar [21]. For the preparation of the control mortar, a reference portland cement is used (CEM I) and a water to cement ratio (W/C) equal to 0.5 and an aggregate (sand) to cement ratio (A/C) equal to 3 are specified. For the preparation of the pozzolanic (SCM) mortar, the same as above water (W) and aggregate (A) contents are used, and cement and pozzolan contents equal to 75% and 25%, respectively, of the control cement content are specified. The mortars are cured under water for a certain period of time until testing (at 28 and 90 days).

According to the above mixture proportions and by applying the Eq. (4.2.5) and (4.3.1) the compressive strengths of the control and SCM mortars are given, respectively, by:

$$f_{c,c} = b / [1 + (W/C)(d_C/d_W) + \varepsilon_{air} (d_C/C)]^2 \qquad (4.3.4)$$

$$f_{c,p} = b / \{1 + [W/(0.75C+k0.25C)](d_C/d_W) + \varepsilon_{air} [d_C/(0.75C+k0.25C)]\}^2 \qquad (4.3.5)$$

By definition, the *activity index* equals to the ratio $f_{c,p}$ / $f_{c,c}$, and thus the following relationships between activity index (AI) and efficiency factor (k, regarding strength) are observed:

$$AI = [(2.8k+8.4)/(k+10.2)]^2 \qquad (4.3.6)$$

$$k = (10.2\sqrt{AI} - 8.4)/(2.8 - \sqrt{AI}) \qquad (4.3.7)$$

EN-450 specifies that the activity index for fly ash shall be not less than 75% and 85%, at 28 and 90 days, respectively [21]. According to Eq. (4.3.7), a k>0.23 for 28 days and a k>0.53 for 90 days are required.

The Eq. (4.3.7) can be used for a faster estimation of the k-values through activity index measurements.

4.3.3 Theoretical approximation of SCM efficiency factor

a. Active silica

In the literature [31, 52-54], there is concertedness that the activity of SCM is mainly based on the fact that they possess significant contents of active constituents, principally reactive silica, that combine with the CH produced from portland cement hydration and form hydration products with binding properties. It is the reactive silica, which is part of the total silica of the supplementary material, that is involved in the hydration reactions producing calcium silicates upon which the strengthening of cement is attributed (see section 3). Reactive silica is non-crystalline silica glass, more particularly present in the amorphous and mostly vitreous part of the supplementary material [55], which can be combined with the lime formed during cement hydration giving increased contents of C-S-H gel [56], unlike crystalline silica that exhibits very low reactivity [57,58]. Richartz [55] had focused his attention on soluble silica stating that the pozzolanic reaction can be expected only from substances or materials whose silica content can dissolve with sufficient rapidity in the alkaline environment of the cement paste, while Bijen [59] noted that in order for the fly ash glass to be activated the links between Si-O-Si have to be broken as fly ash does not dissolve, contrary to slag, but actually decomposes.

In earlier methods, reactive silica was estimated as the difference between the total silica and free silica [60,61], which were determined after fusion by gravimetric method before and after treating the fly ash with hydrochloric acid. Sivapullaiah et al. [62] also used the gravimetric method to determine the reactive silica indirectly as acid (HCl 1+1) soluble silica, giving surprisingly low values for different fly ashes. The amounts obtained by this method were even more than those present even in portland cement [60,61] with the difference that the concentration of acid was higher than that used for portland cement, mortar, concrete (where only a dilute HCl of 3N is used) [63]. Another method put forward by Mehta [64], established the concept of the ‘silica activity index’ meaning the percentage of available silica that is dissolved in an excess of boiling 0.5 M NaOH solution during a 3-min extraction period. Simpler methods have been proposed [65], based on the titration of sample suspensions with methylene blue. The amount of methylene blue required to produce a color change in the solution can be used as an index of the amorphousness of the silica contained in the ash. Paya et al. [66] recently proposed a rapid method for the determination of amorphous silica in rice husk ashes, based on bringing the siliceous non-crystalline fraction of the pozzolan into solution as glycerosilicate by treating the test material with glycerol. The results gave satisfactory concordance with the reference method.

b. Determination of reactive silica content

According to European Standard prEN 197-1 [13], reactive silica is defined as the fraction of the silicon dioxide which is soluble after treatment with hydrochloric acid and with boiling potassium hydroxide solution. The European Standard EN 196-2 was used to determine the active silica contents of all SCM used in this work. This standard specifies that the reactive silica content in pozzolans is determined by subtracting from the total silica content of the pozzolan, the fraction that is contained in the insoluble residue. To be more specific, the percentage of the active silica of a pozzolan was estimated as the difference between the total amount of silica and the silica present in the insoluble residue, as this is determined after treatment with hydrochloric acid and a 25 % boiling potassium hydroxide solution in a 4-hour extraction.

In a brief description, sintering of 1 g of the dried sample with Na_2O_2 is followed by a persistent treatment with hydrochloric acid until the final solution is filtered. The content of the filter paper is burned in an electric furnace for an hour at 1100^0 C giving the percentage of the total silica contained in the pozzolan. The same procedure was followed for determining the silica present in the insoluble residue with the difference that the sintering involves the previous extracted residue.

Although the particular method is considered time consuming and requires increased caution by the analyst, it provides more reliable results when compared with resembling methods. Emphasis must be given in the sample preparation stage, as pozzolans with high carbon content (or higher loss on ignition, LOI) must be sintered in temperatures slightly higher than the reference one. Unsuccessful sintering, accompanied by incomplete nitrate tests (required both in the estimation of total silica and insoluble residue contents) may result in the presence of impurities in the silica sediment. In such cases the burnt sample must be further treated with hydrofluoric and sulfuric acid making the procedure even more tedious.

By following the above method, the reactive silica contents of the various SCM used in this work are determined and given in Table 3.2.2, section 3.

c. Relationship between k-value and active silica

It is evident that although several authors have attempted to connect the pozzolanic effect with a number of parameters such as, fineness [67,68], water to powder ratio [69], curing temperature [69,70] and alkalinity of the pore solution [71], it seems to be a lack in the literature regarding the effect of the reactive silica content on their pozzolanicity and behavior as additives in cement and concrete. Even proposed mechanisms for the quantification of the pozzolanic activity [72,73] have not produced a relation between the amount of soluble silica of the examined admixtures and their potential activity. The present investigation aims at filling this gap by introducing a relationship between the reactive silica amount of different SCM and their corresponding k-values, estimated both for mechanical and durability properties. This will lead to a more safe prediction of the quantity, but most of all the quality of the SCM used in the concrete mix design so that the final product will meet certain specified requirements (e.g. strength, service life time, etc.).

In an SCM-cement system, the CSH-content will also be the most critical parameter in strength development. In a previous work [46,47,50,51] was fully established that, as time proceeds, i.e., after 1 year, the following expression can be obtained, giving an estimation for the maximum k-value:

$$k_{max} = \gamma_{S,P}\, f_{S,P} / f_{S,K} \qquad (4.3.8)$$

As a general conclusion, the Eq. (4.3.8) can be applied for a first approximation of the k-value of the artificial SCM, such as fly ash, slag, silica fume, and some thermal treated natural materials, such as metakaolin. In the case of multicomponent use (simultaneous use of various SCM) in the concrete production, the sum of the active silica of the materials can be introduced in Eq. (4.3.8). However, a significant overestimation was observed for the natural materials [47]. This exception can be attributed either to the formation of a weaker CSH component or to errors in active silica measurement.

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 $Ca(OH)_2$ 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 CO_2 and its reaction with the $Ca(OH)_2$ of the concrete mass, or by a combination of these two mechanisms, in which the second mechanism accelerates the first, Fig. 5.1.1.

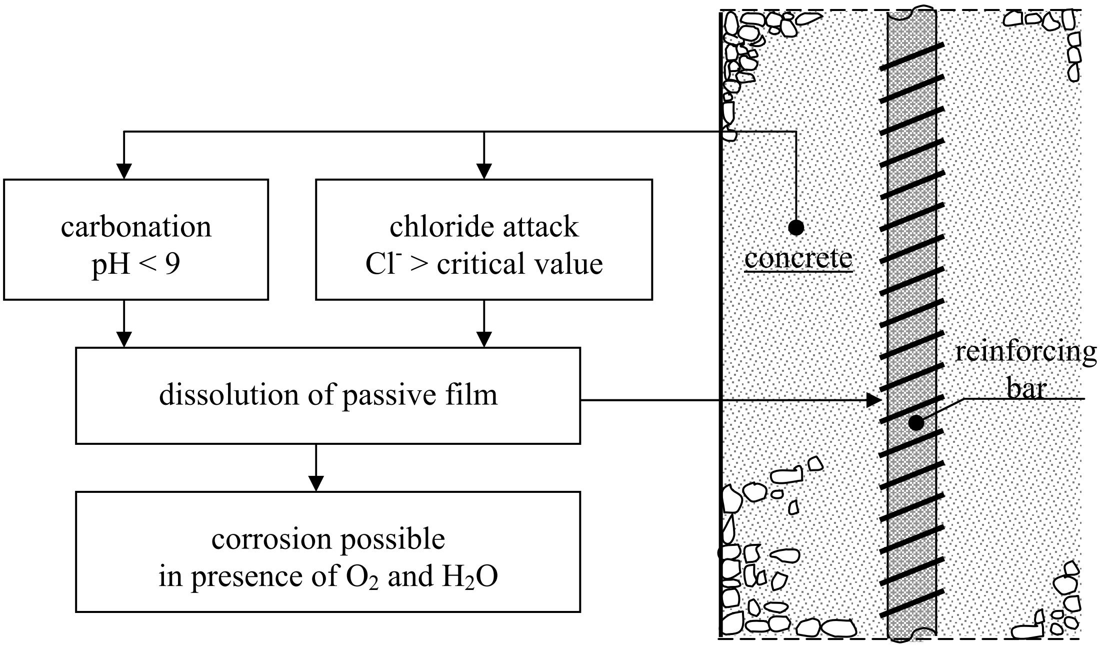

Figure 5.1.1 Initiation mechanisms of corrosion in concrete.

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 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 CO_2 include not only $Ca(OH)_2$, but also the main strength component of cement paste CSH, and the unhydrated constituents of C_3S and C_2S [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 CO_2 through the pores; second, it provides a medium for reaction between CO_2 and $Ca(OH)_2$.

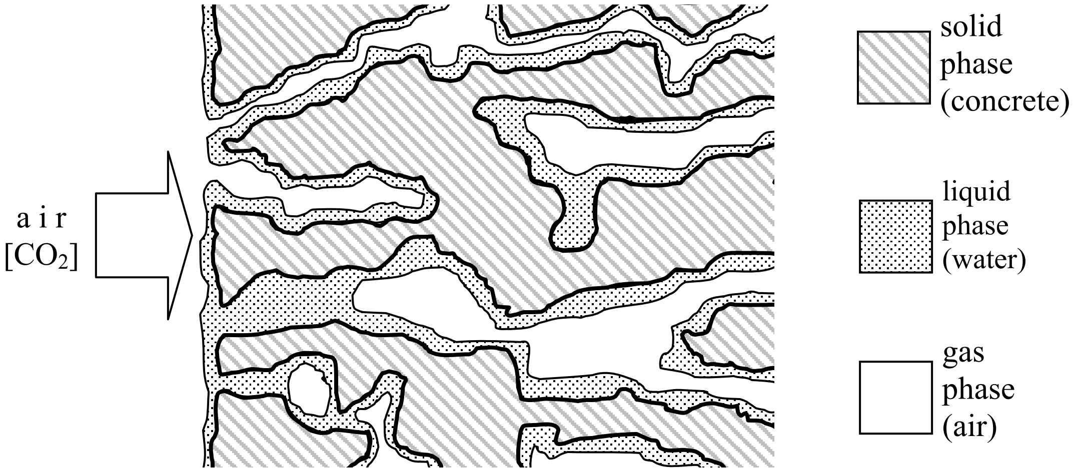

Figure 5.1.2 Schematic representation of concrete carbonation.

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_2 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_2 becomes very slow.

The *overall reaction* between solid $Ca(OH)_2$ (s) and diffused gaseous CO_2 (g),

$$Ca(OH)_2\,(s) + CO_2\,(g) \rightarrow CaCO_3\,(s) + H_2O \qquad (5.1.1)$$

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 $Ca(OH)_2$ dissolution step and other elementary steps:

$$Ca(OH)_2\,(s) \leftrightarrow Ca^{2+}\,(aq) + 2OH^-\,(aq) \qquad (5.1.2)$$

$$CO_2\,(g) \rightarrow CO_2\,(aq) \qquad (5.1.3)$$

$$CO_2\,(aq) + OH^-\,(aq) \rightarrow HCO_3^-\,(aq) \qquad (5.1.4)$$

$$HCO_3^-\,(aq) + OH^-\,(aq) \rightarrow CO_3^{2-}\,(aq) + H_2O \qquad (5.1.5)$$

$$Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \rightarrow CaCO_3\,(s) \qquad (5.1.6)$$

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:

$$C_3S_2H_3 + 3CO_2 \rightarrow (C\overline{C})_3S_2H_3 \qquad (5.1.7)$$

$$C_3S + 3CO_2 + nH_2O \rightarrow SiO_2.nH_2O + 3CaCO_3 \qquad (5.1.8)$$

$$C_2S + 2CO_2 + nH_2O \rightarrow SiO_2.nH_2O + 2CaCO_3 \qquad (5.1.9)$$

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_2 in the gas-phase of pores, its dissolution in the aqueous film of these pores, the dissolution of solid $Ca(OH)_2$ in pore water, its ultimate reaction with the dissolved CO_2, and the reaction of CO_2 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≥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]:

$$x_c = \sqrt{\frac{2D_{e,CO2}(CO_2 / 100)t}{0.33CH + 0.214CSH}} \qquad (5.2.1)$$

where, CO_2: the *CO_2-content* in the ambient air at the concrete surface (%), and $D_{e,CO2}$: the *effective diffusivity* of CO_2 in carbonated concrete (m^2/s). CO_2-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]:

$$D_{e,CO2} = 6.1.10^{-6}\left(\frac{\varepsilon_c - \varepsilon_{air}}{1-\frac{A}{d_A}-\varepsilon_{air}}\right)^3 (1-RH/100)^{2.2} \qquad (5.2.2)$$

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≥55%):

$$t_{cr,carb} = \frac{(0.33CH + 0.214CSH)c^2}{2D_{e,CO2}(CO_2/100)} \qquad (5.2.3)$$

- **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.**

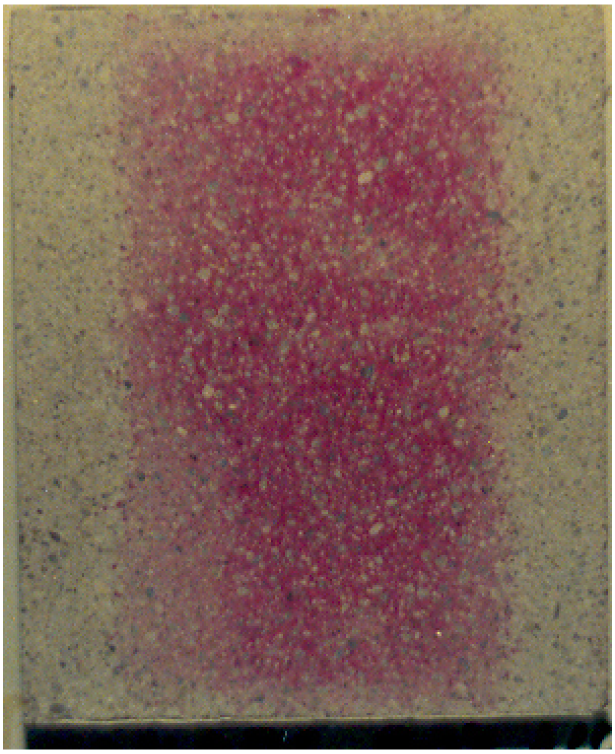

Figure 5.2.1 Separation of carbonated (colourless) from a non-carbonated area (pink) in a typical concrete spraying by phenolophthalein solution.

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 λ [78]:

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

$$x_c = \lambda \sqrt{\frac{2D_{e,CO2}(CO_2/100)t}{0.33CH + 0.214CSH}} \tag{5.2.5}$$

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 λ^2, i.e.,

$$t_{cr,\,carb} = \frac{(0.33CH + 0.214CSH)c^2}{2D_{e,CO2}(CO_2/100)\lambda^2} \tag{5.2.6}$$

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.

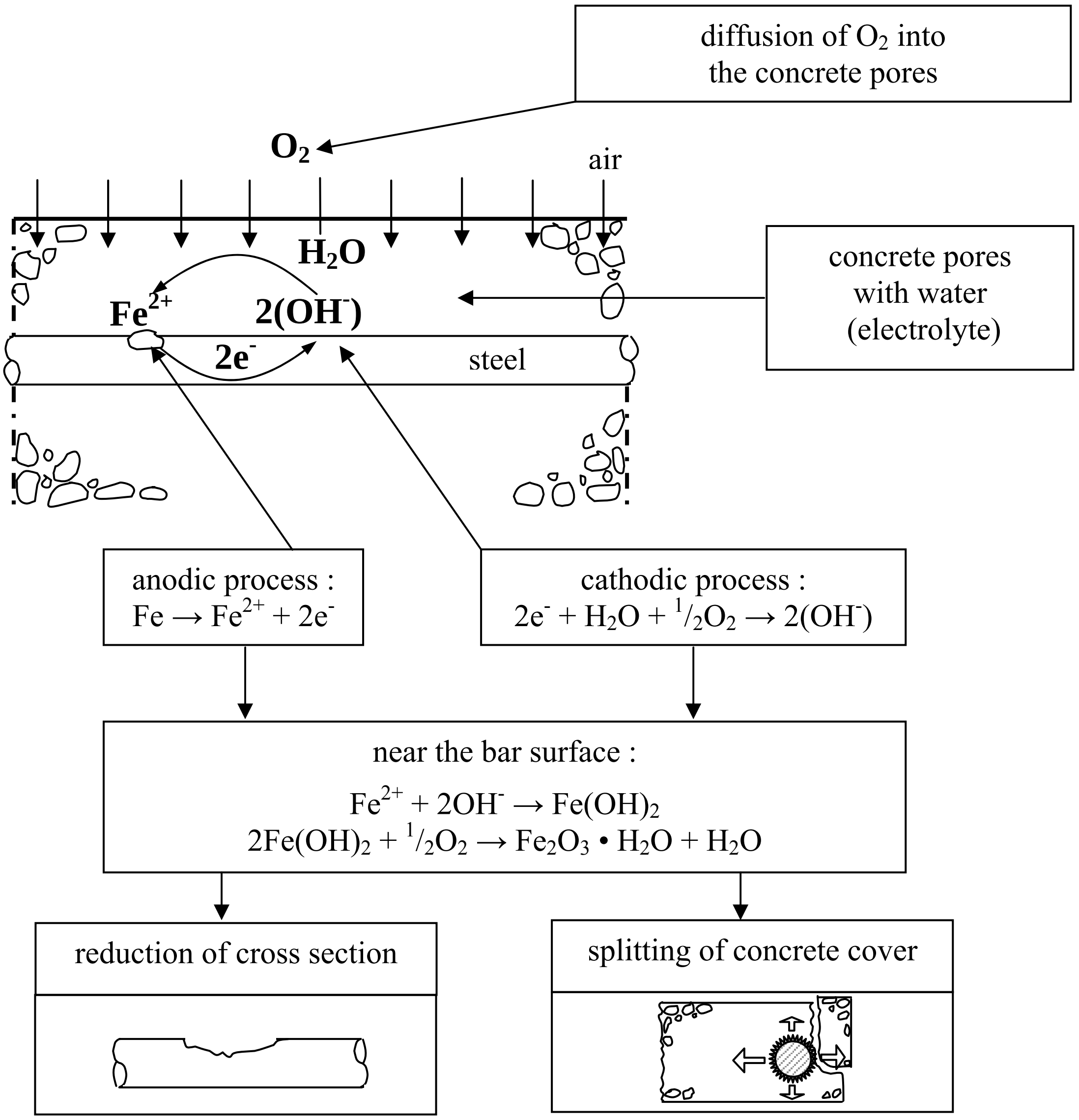

Figure 5.3.1 Mechanism and results of corrosion of steel in concrete.

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:

Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (5.3.1)

Cathode: $2e^- + ½O_2 + H_2O \rightarrow 2OH^-$ (5.3.2)

Near the surface: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (black rust) (5.3.3)

$2Fe(OH)_2 + ½O_2 \rightarrow Fe_2O_3.H_2O$ (red rust) $+ H_2O$ (5.3.4)

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 Fe^{2+} but is Fe_3O_4, which is deposited at the metal surface in a thin and dence 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.

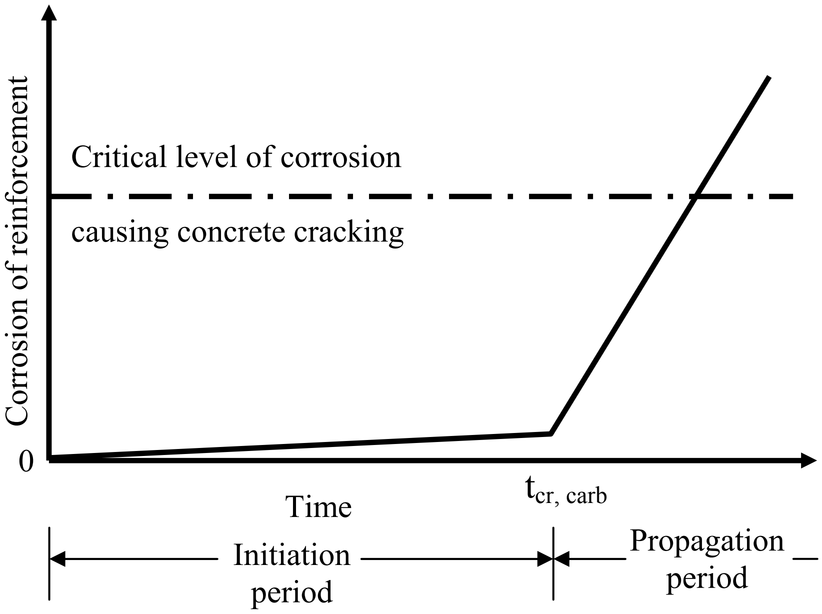

Figure 5.3.2 The two stages for corrosion damage in reinforced concrete.

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 ^{o}C) and 55%<RH<95%, the rate of corrosion, q_c (10^{-4} g/cm^2/yr), of the steel bar in concrete can be approached by the following empirical formula:

$$q_c = 65\ (RH/100) - 35 \tag{5.3.5}$$

The critical amount of corrosion, Q_{cr} (10^{-4} g/cm^2), 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]:

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

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

$$\boxed{t_{pr,carb} = [6\ (1 + 0.2\ c)^{0.85}] / [65\ (RH/100) - 35] \qquad (5.3.7)}$$

Finally, the service lifetime, Z_{carb} (in years), as regards the carbonation-induced corrosion of the concrete reinforcement, is the total sum of the two periods ($t_{cr,carb}$ has to be converted in years dividing by 31,557,600s/yr):

$$Z_{carb} = t_{cr,carb} + t_{pr,carb} \tag{5.3.8}$$

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, 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
1 No risk of corrosion or attack					
X0	For concrete with reinforcement or embedded metal: Very dry	Concrete inside buildings with very low air humidity	<45	1	0
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	Concrete inside buildings with low air humidity	45-65	3	1
	Permanent wet	Concrete permanently submerged in water	>98	0	1
XC2	Wet, rarely dry	Concrete surfaces subject to long-term water contact, many foundations	90-98	1	2
XC3	Moderate humidity	Concrete inside buildings with moderate or high air humidity, external concrete sheltered from rain	65-85	2	3
XC4	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 μm, and as the corrosion rate is about 0.3 μm/yr [10,87] in this RH region, the propagation period is $t_{pr,carb}>100$ 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≥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%≤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%≤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 μm/yr [10,87], fact that gives propagation periods of the order of 5-20 years (as 100 μm 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%≤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

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_2, O_2, 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. $Ca(OH)_2$ 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 of 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 (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.

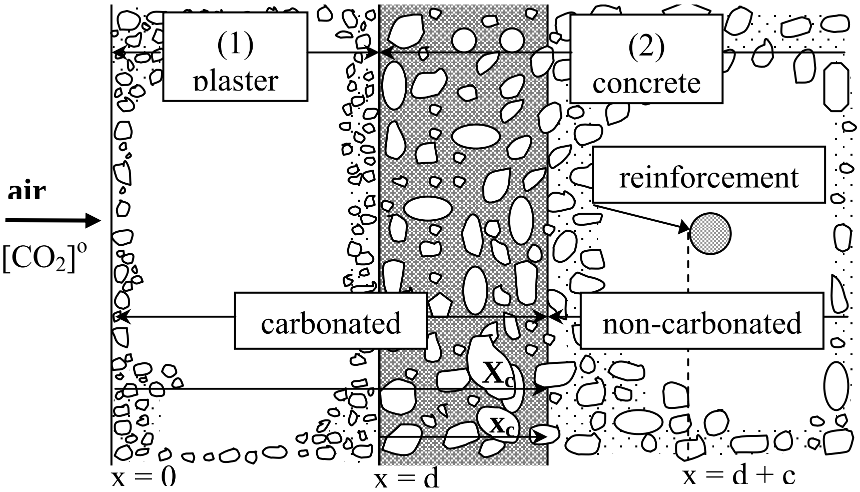

Figure 5.4.1 Schematic illustration of concrete carbonation in the presence of mortar coating ($t>t_d$).

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:

$$t_d = \frac{(0.33CH^{(1)} + 0.214CSH^{(1)})d^2}{2D_{e,CO2}^{(1)}(CO_2/100)} \tag{5.4.1}$$

For RH<55% this time has to be corrected divided it by the factor λ^2, see section 5.2.2. So, during the first phase, i.e. for $0 \le t \le t_d$, 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:

$$d^2[CO_2]/dx^2 = 0 \qquad \text{for } 0 \le x \le X_c \tag{5.4.2}$$

within the coating ($0 \le x \le d$), which is fully carbonated, and within the carbonated region of concrete ($d \le x \le X_c$). 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:

$$x_c = \sqrt{\frac{2D_{e,CO2}^{(2)}(CO_2/100)}{0.33CH^{(2)} + 0.214CSH^{(2)}}(t - t_d) + d^2\left(\frac{D_{e,CO2}^{(2)}}{D_{e,CO2}^{(1)}}\right)^2} - \mathrm{d}\frac{D_{e,CO2}^{(2)}}{D_{e,CO2}^{(1)}} \tag{5.4.3}$$

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:

$$t_{cr,\,carb} = t_d + \frac{(0.33CH^{(2)} + 0.214CSH^{(2)})(c^2 + 2dcD_{e,CO2}^{(2)}/D_{e,CO2}^{(1)})}{2D_{e,CO2}^{(2)}(CO_2/100)} \tag{5.4.4}$$

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, $D^{(1)}_{e,CO2}$, 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 $Ca(OH)_2$ 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 $Ca(OH)_2$ will react with the new 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]:

$$x_c = \sqrt{\frac{2D^{(2)}_{e,CO2}(CO_2/100)}{0.33CH^{(2)} + 0.214CSH^{(2)}}(t - t_d) + \left(d\,\frac{D^{(2)}_{e,CO2}}{D^{(1)}_{e,CO2}} + x_{c,a} \right)^2} - \mathrm{d}\,\frac{D^{(2)}_{e,CO2}}{D^{(1)}_{e,CO2}} \qquad (5.4.5)$$

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

$$t_{cr,\,carb} = t_d + \frac{(0.33CH^{(2)} + 0.214CSH^{(2)})[c^2 + 2d(c - x_{c,a})D^{(2)}_{e,CO2}/D^{(1)}_{e,CO2} - x^2_{c,a}]}{2D^{(2)}_{e,CO2}(CO_2/100)} \qquad (5.4.6)$$

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 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 (kg/m^3 mortar) the lime content in the mixture, defining as lime the dry $Ca(OH)_2$ without excess water (in a water-saturated, surface-dry form), and by d_L the mass density of lime (kg/m^3). The following mass balance equation has then to be fulfilled:

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

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

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

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_{MOR} (kg/m^3), is given by:

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

The $CH^{(1)}$ and $CSH^{(1)}$ 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 CO_2 in a carbonated mortar coating, $D^{(1)}_{e,CO2}$, 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 confirm to EN 459-1 [93].

6. CONCRETE SERVICE LIFE REGARDING CHLORIDE PENETRATION

6.1 Physicochemical considerations

6.1.1 The significance of the problem

Numerous surveys have indicated that chloride ions (Cl^-), originating from de-icing salts or seawater, are the primary cause of reinforcing steel corrosion in highways and marine or coastal structures [1,4,7-10]. The chlorides that transported through the concrete pore network and microcracks depassivate the oxide film covering the reinforcing steel and accelerate the reaction of corrosion and concrete deterioration, see Fig. 6.1.1. Even high-performance concrete may not necessarily ensure long-term durability in a severe environment unless it is designed for dimensional stability and soundness [5].

Figure 6.1.1 Photo of deteriorated concrete element due to reinforcement corrosion induced by chloride attack.

Chloride penetration is a process which takes place in totally or partly water-filled pores. This is the main reason that as a process is much slower than carbonation, where CO_2 molecule may penetrate faster via air-filled pores.

6.1.2 Sources of chlorides in concrete

Concrete is a porous material. Its solid skeleton consists of gravel and sand, bound together by the hardened cement paste. Its pores are partly or completely filled with water. The degree of pore saturation depends on their size and on relative humidity of the environment.

The source of chlorides in concrete may be *internal or external*. In the former and less common case, chlorides are present in the concrete from the very beginning. This is the case if chloride-containing admixtures are used in the concrete mix (e.g. $CaCl_2$ is a main constituent of many admixtures added to accelerate the setting and hardening of concrete), or if seawater or beach aggregates are used in the concrete construction in coastal or marine regions away from supplies of nonsaline materials.

In most cases of reinforcement corrosion due to chlorides, the source of chlorides is external. The use of de-icing salts in roads and highways during the winter is widespread in cold climates. Chlorides in these salts, dissolved in water, find easily their way into the concrete of bridge decks and abutments, into that of parking garages, etc. In marine environments, concrete is in contact with sea-water, continuously in the submerged parts or periodically in the tidal and splash zone. In coastal areas, air and mist blown inland from the sea are laden with salts. Chlorides that reach the concrete surface in this or the other way, enter the pore system either by diffusion in stationary pore water or by capillary suction of the surface water in which they are dissolved, or by combination of both transport mechanisms.

6.1.3 Main physicochemical processes

Almost in the majority of papers, chloride transport in concrete is modelled using the *Fick's second law of diffusion neglecting the chloride interaction with the solid phase*. However, it is widely proved that chlorides are bound from concrete components in a percentage 30-60% depending on cementitious materials' composition and content [31,81]. Several field studies in recent years have indicated that the use of this law is not applicable to long-term chloride transport in concrete, calculating very often a decreasing chloride transport coefficient in time [94]. It is widely accepted that the transport behaviour of chloride ions in concrete is a more complex and complicated process than can be described by Fick's law of diffusion [95-97]. This approach, therefore, can be characterized as semi-empirical, resulting in the calculation of an "apparent" effective diffusivity. Thus, a term of adsorption-reaction of chlorides in concrete has definitely to be considered in an accurate model, see Fig. 6.1.2. Otherwise, using only the term of diffusion, despite satisfactory approach of the experimental results, the yielded "diffusivity" coefficient is not valid for other applications and predictions.

There is a generally good correlation between C_3A-content (or C_4AF when there is lack of C_3A-phase) and chloride binding capacity. There is also evidence for the binding of chlorides in CSH gel, possibly in interlayer space [98]. The Na^+ ions can be bound in CSH gel lattice [99], especially when the C/S ratio is low [20]. Several secondary chloride-calcium compounds have also been reported [100].

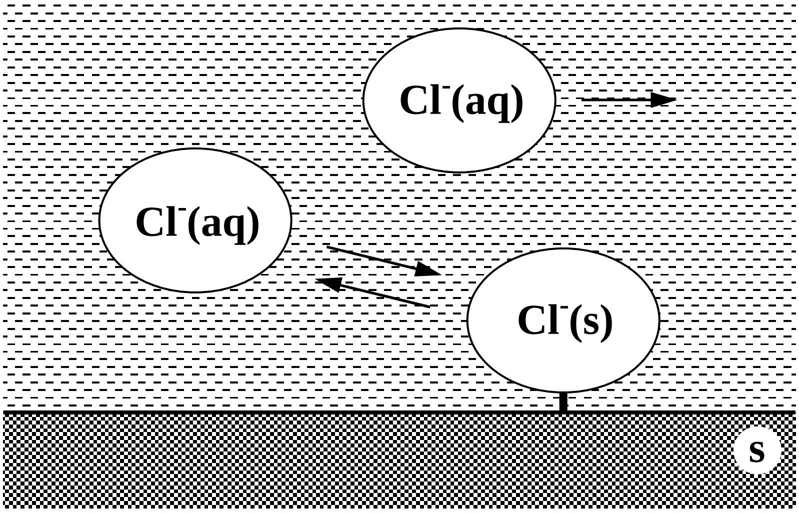

Figure 6.1.2 Schematic representation of chloride ion diffusion in water-saturated pores of concrete and its partial binding from the solid phase of concrete.

In addition to the chemical binding, the effects of ionic interaction, lagging motion of cations and formation of an electrical double layer on the solid surface all play an important role in the transport of chloride ions in concrete [96]. The relationship between bound and free chlorides is non-linear and may be expressed by the Langmuir equation [101], the Freundlich equation or the modified BET equation [97]. Of these, the Langmuir equation is both fundamental and easier to use in practical applications.

6.2 Theoretical model

6.2.1 Mass balances

Pereira and Hegedus [101] were the first to identify and model *chloride diffusion and reaction* in fully saturated concrete as *a Langmuirian equilibrium process coupled with Fickian diffusion*. Furthermore, Papadakis et al. [102,103] generalized this pioneering effort, offering an alternative simpler, yet equally accurate, numerical and analytical solution. By introducing a chloride-solid phase interaction term in the equations the calculation of an *"intrinsic" effective diffusivity* is possible. The *physicochemical processes* of diffusion of Cl^- in the aqueous phase of pores, their adsorption and binding in the solid phase of concrete, and their desorption therefrom are described by a nonlinear partial differential equation for the concentration of Cl^- in the aqueous phase $[Cl^-(aq)]$ (in kg/m^3 pore solution), from which that of Cl^- bound in the solid phase $[Cl^-(s)]$ (kg/m^3 concrete) can be computed algebraically:

$$\frac{\partial [Cl^-(aq)]}{\partial t} = \frac{D_{e,Cl^-}(1+K_{eq}[Cl^-(aq)])^2}{K_{eq}[Cl^-(s)]_{sat} + \varepsilon(1+K_{eq}[Cl^-(aq)])^2} \frac{\partial^2 [Cl^-(aq)]}{\partial x^2} \quad (6.2.1)$$

$$[Cl^-(s)] = \frac{K_{eq}[Cl^-(aq)]}{1+K_{eq}[Cl^-(aq)]}[Cl^-(s)]_{sat} \quad (6.2.2)$$

initial condition: $[Cl^-(aq)] = [Cl^-(aq)]_{in}$ at $t = 0$ (initial concentration) (6.2.3)

boundary conditions: $[Cl^-(aq)] = [Cl^-(aq)]_0$ at $x = 0$ (concrete surface) (6.2.4a)

$\partial[Cl^-(aq)] / \partial x = 0$ at $x = M$ (axis of symmetry) (6.2.4b)

The total chloride concentration [Cl^-(total)] (in kg/m^3 concrete) is the sum of chlorides in solid and aqueous solution, i.e., (ε[Cl^-(aq)]+[Cl^-(s)]). In the above equations, x is the distance from the concrete surface (m), t is the time (s), D_{e,Cl^-} denotes the intrinsic effective diffusivity of Cl^- in concrete (m^2/s), K_{eq} the equilibrium constant for Cl^- binding (m^3 of pore volume/kg), [Cl^-(s)]$_{sat}$ the saturation concentration of Cl^- in the solid phase (kg/m^3 concrete), and ε the concrete porosity (m^3 pore volume/m^3 concrete). As observed from Eq. (6.2.2), the chloride binding capacity depends both on [Cl^-(s)]$_{sat}$ (content of sites which can bind chlorides) and K_{eq} (ratio of adsorption to desorption rate constants).

As observed from Eq. (6.2.1), chloride ingress is retarded as D_{e,Cl^-} decreases, [Cl^-(s)]$_{sat}$ increases, or K_{eq} increases. When an SCM is added in concrete, chloride binding capacity increases, as experimental results showed ([81], higher total chloride content in a thin layer near the external mortar surface). This may be attributed to higher CSH content, especially that with lower C/S ratio, which can bind Na^+ ions and, therefore, the accompanying Cl^-. On the other hand, the pore restructuring due to pozzolanic products may decrease intrinsic diffusivity as well. As observed by scanning electron micrograph [81], a fine network of pozzolanic product (CSH) has been created in the middle of a capillary pore acting as a trap for chlorides. Using atomic force microscopy [104], it was found that the internal surface of the SCM-cement pastes presents small spheroid bulges giving an additional roughness.

The picture is different when a non-interacting molecule diffuses in a concrete incorporating SCM, as observed from carbonation results [31,81]. The ratio of oxygen to chloride diffusion coefficients was found constant for portland pastes of high W/C ratio but can attain high values for fine-textured blended cement pastes which have not suffered drying/carbonation [105]. It has also been reported [106] that this ratio increases as W/C ratio decreases. Also, it was found [107] that in the presence of chlorides the diffusivity of dissolved oxygen into saturated concretes decreases over and above the decrease of oxygen solubility in solution. It has also been reported [108], that up to a fly ash level of 33% the intrinsic air permeability remains fairly constant and then is higher compared to the control. The apparent chloride diffusion coefficient was found to decrease by a factor of 7. Chloride binding capacity increases by a factor of 4 and then remains constant. It seems, therefore, that chloride binding capacity is the determining factor in improving resistance to chloride ingress.

6.2.2 Parameter estimation

In the case of "complete" hydration and pozzolanic action, and for typical composition of the cementing materials, the *total porosity of concrete* can be calculated from Eq. (3.2.17), (3.2.28), (3.2.35) or (3.2.43).

The *intrinsic effective diffusivity* of Cl^- in concrete (m^2/s), can be estimated by the following semi-empirical equation [31,81, for NaCl; for $CaCl_2$ the numerator is $2x10^{-10}$]:

$$D_{e,Cl^-} = \frac{2.4.10^{-10}}{\left(\frac{K + CS + \sum(kP_{ACT})}{d_C} + \frac{W}{d_W}\right)^2}(\varepsilon_{eff})^{3.5} \qquad (6.2.5)$$

P_{ACT} is the active content of each SCM added either as cement constituent or as concrete addition (kg/m^3), having an efficiency factor k. This is given in the previous section 3, as S_{ACT}, F_{ACT}, P_{ACT}, or SL_{ACT}. In Eq. (6.2.5), k is the *efficiency factors regarding chloride penetration* for each SCM added either as cement constituent or as concrete addition (see Table 6.2.1 for experimental values). Parameter ε_{eff} is an *effective*, for diffusion, porosity, calculated as follows:

$$\varepsilon_{eff} = W/d_W - 0.226\ 10^{-3}\ \{K+CS + \sum(kP_{ACT})\} \qquad (6.2.6)$$

If *sea attack* concerns, the *chloride concentration in the aqueous solution* at the concrete surface, $[Cl^-(aq)]_0$ (kg/m^3 pore solution), depends on the sea, e.g., Atlantic Ocean and Mediterranean Sea: 20 kg/m^3, North Sea: 16 kg/m^3, Baltic Sea: 4 kg/m^3.

In the case of de-icing salts, the estimation of $[Cl^-(aq)]_0$ involves uncertainties due to many unknown parameters (frequency and quantity of salt spreading, amount of available water from rain or melted snow for salt dissolution, etc.). As a matter of fact, high Cl^- concentrations of 100 kg /m^3 are usual. As the salt spreading takes place only a few months per year and moreover due to washing by rain the chloride surface concentration decreases, an exposure

Table 6.2.1 Efficiency factors (k-values) regarding chloride penetration for various supplementary cementing materials [31,81]*.

	Cementitious/ pozzolanic materials	Chloride resistance
1	Portland clinker	1
2	Blast furnace slag	2.2
3	Silica fume	6
4	Pozzolana (natural)	1
5	Metakaolin	5
6	Siliceous fly ash	3
7	Calcareous fly ash	2.2
8	Burnt shale	2.2
9	Limestone	0.1
10	Various SCM for CEM II	2.2
11	Various SCM for CEM IV	3
12	Various SCM for CEM V	3

* All these SCM were ground prior to use up to a fineness of 400±20 m^2/kg according to Blaine's test.

equivalent to a concentration of 20 kg/m^3 continuously all year round can be adopted as a first approximation. However, a more realistic approach based on statistical data should be sought.

Another important conclusion from parametric analyses on chloride penetration [102] should be mentioned here. Let us suppose that the exposure of the concrete surface to chlorides is not continuous but *periodic*, dividing the total lifetime into a number of intervals of length T, during one part, ρT, of which the surface is considered to be exposed to chloride ingress, while during the rest, (1-ρ)T, it is not. Pore saturation conditions, however, were not considered to be affected by the change in exposure conditions. Results showed that *the free chloride concentration* at any time and distance ($[Cl^-(aq)]_\rho$) is *independent of total duration T* of the exposure-nonexposure cycle, increases linearly with the *"exposure ratio", ρ,* and it can be calculated by multiplying that of the continuous exposure ($[Cl^-(aq)]_{\rho=1}$) by the ρ, i.e.:

$$[Cl^-(aq)]_\rho = \rho\, [Cl^-(aq)]_{\rho=1} \qquad (6.2.7)$$

The above conclusion is very important and it can be applied in the case of de-icing salts. In other words, if the exposure ratio is ρ=0.2 (1/5 of the year) for concrete subjected to contact with water containing chlorides originating from de-icing salts of a concentration of 100 kg/m^3, the free-Cl$^-$ concentration will be the 0.2 of that of the continuous exposure.

Parameters $[Cl^-(s)]_{sat}$ and K_{eq} can be determined from chloride binding isotherms. An experimental approach described in **Appendix A** was followed. The *equilibrium constant for Cl$^-$ binding* was found fairly constant for all mixtures (K_{eq} = 0.1 m^3 of pore volume/kg Cl$^-$). For *saturation concentration of Cl$^-$ in the solid phase*, the following empirical expression may be used [31,81,103]:

$$[Cl^-(s)]_{sat} = 8.8\ 10^{-3}\ \{K+CS + \sum(kP_{ACT})\} \tag{6.2.8}$$

$$K_{eq} = 0.1\ m^3 \text{ pore volume/kg } Cl^- \tag{6.2.9}$$

6.2.3 Chloride threshold for reinforcement corrosion

A way of threshold expression is by measurement the *total chloride ion content in concrete required for the onset of reinforcement corrosion*. This approach embodies inaccuracies because only the free chlorides present in pore solution cause corrosion.

However, it is very often reported that **if the total chloride content is more than 0.4% bw of cement, the steel is activated and corrosion may occur**. It has been demonstrated [109] that the chloride threshold for uncracked SRPC (sulphate-resistant portland cement) concrete with low W/C ratio (0.3-0.5) is in the range of 1-1.3% total chloride bw of binder, for SRPC concrete with 5% SF in binder is 0.8-1.0%, and with 10-20% fly ash in the binder is about 0.7%. Moreover, it is generally accepted [10] the following description of the corrosion risk:

- less than 0.4% chloride by mass of cement: low risk
- 0.4 – 1.0% chloride by mass of cement: medium risk
- greater than 1.0% chloride by mass of cement: high risk

In the case of use of additions the binder quantity has rather to be taken into account. Multiplying by the cementitious materials' content in concrete, a lower and an upper limit could be defined:

$$[Cl^-(total)]_{cr,min} = 0.004\ \{K+CS + \sum(P_{ACT})\}\ \text{kg total chlorides/ m}^3\ \text{concrete} \qquad (6.2.10)$$

$$[Cl^-(total)]_{cr,max} = 0.012\ \{K+CS + \sum(P_{ACT})\}\ \text{kg total chlorides/ m}^3\ \text{concrete} \qquad (6.2.11)$$

However, for final design a mean value of critical total chloride content for corrosion of reinforcement is proposed:

$$\boxed{[Cl^-(total)]_{cr} = 0.008\ \{K+CS + \sum(P_{ACT})\}\ \text{kg total chlorides/ m}^3\ \text{concrete} \qquad (6.2.12)}$$

6.2.4 *Model solution*

Eq. (6.2.1) can be solved only *numerically*, e.g., using a finite difference or element method, for the given initial and boundary conditions, Eqs. (6.2.3)-(6.2.4). The solution gives the free-Cl^- concentration, $[Cl^-(aq)]$, for various distances x in the concrete mass and at various ages, t, and by applying Eq. (6.2.2), the bound-Cl^- concentration, $[Cl^-(s)]$ is calculated. The total chloride concentration $[Cl^-(total)]$ (in kg/m^3 concrete) is the sum of chlorides in solid and aqueous solution, i.e., $(\varepsilon[Cl^-(aq)]+[Cl^-(s)])$. The solution allows estimation of the time (**critical time for chloride-induced corrosion, $t_{cr,chlor}$**) required for the total chloride concentration surrounding the reinforcement (located at a distance c from surface- *cover*) to increase over the threshold for depassivation, $[Cl^-(total)]_{cr}$. We can state the following:

The service lifetime of a structure, regarding chloride penetration, is at least $t_{cr,chlor}$.

Afterwards, the propagation of corrosion process takes place at a rate that depends strongly on the availability of both oxygen and water. The following sections offer a qualitative prediction of the propagation period. Only as a first approximation, the corrosion rates presented in the carbonation section may be used.

6.3 Corrosion of the reinforcement in chloride-rich concrete

6.3.1 Estimation of the corrosion propagation period

The anodic reaction is of particular interest in the case of chloride-rich concrete, i.e., when the Cl^- concentration has exceeded the critical value for corrosion at the reinforcement area [1,7,10, 110]. The anodic process consists of the following steps, see also Fig. 6.3.1:

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{6.3.1}$$

$$Fe^{2+} + 2Cl^- \rightarrow FeCl_2 \tag{6.3.2}$$

$$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2Cl^- \tag{6.3.3}$$

There follows a consequent recycling of the liberated chloride ions. Although corrosion product is being produced at this particular point of bar (pitting corrosion) so too H^+ and Cl^-. The increased acidity of the anodic area helps to prevent precipitation of corrosion product and it encourages further oxidation of the iron bar.

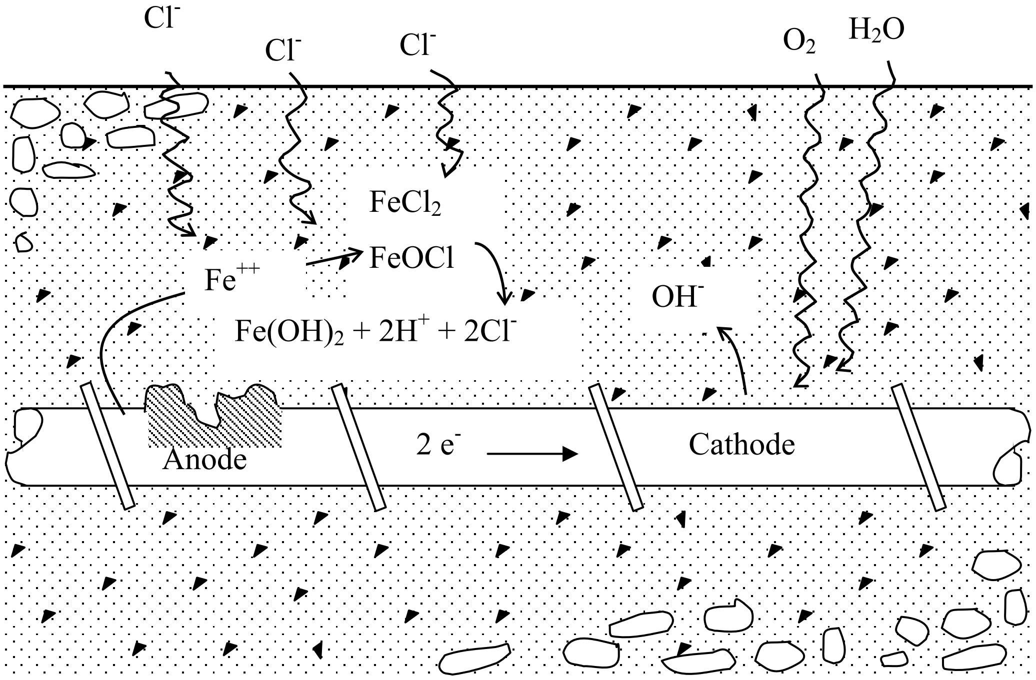

Figure 6.3.1 Mechanisms and results of pitting corrosion in a chloride-rich environment.

However, the rate of corrosion is influenced by the availability of O_2 and H_2O at the cathode, that is not straightforward because even low rates of O_2 supply may lead to a severe pitting corrosion. This effect occurs because the anodic sites may be localized but the corresponding cathodic sites may be spread out over a wide area. The cumulative effect of even low rates of O_2 supply to large cathodes may be significant. As the corrosion product is discouraged from precipitation, and due to the existence of highly active and localized anodic sites, a severe pitting corrosion may occur without an earlier warning through visible signs at the surrounding concrete. This can lead to rapid loss of cross-section and critically reduce the load bearing capacity of the reinforced concrete member. When cracks do develop, the corrosion product will then be deposited along the crack. By the time rust staining becomes apparent at the surface, the extent of reinforcement deterioration may be structurally significant.

The possible mechanism of chloride ion interaction with the reinforcement and passive layer has not been fully resolved. Moreover, the estimation of propagation period and the definition of the end of the service life due to chloride-induced corrosion are also contain a lot of uncertainties [84-86, 111-113]. Therefore, as in the case of carbonation, *the time* $t_{cr,chlor}$ *required for* Cl^- *to exceed the critical value at the concrete cover c can be considered in good approximation as a narrow lower bound to the service life of reinforced concrete.*

6.3.2 Relationship with EN 206

The passivity of the reinforcement is depended on the stability of the passive film formed on it when the steel is found in the alkaline environment of the fresh concrete. This passive film is rendered ineffective when the Cl^- level in the surrounding concrete exceeds a critical value. The internal sources of Cl^- are currently limited to tolerable levels by specification. For example, the European Standard EN 206-1 [12] limits the chloride content in a range of 0.1-0.4% of cement by mass in the case of reinforced concrete. Especially, the chloride content of a concrete, expressed as the percentage of chloride ions by mass of cement, shall not exceed the value for the selected class given in Table 6.3.1. The strictest limitations apply to prestressed concrete. Aggregate standards also limit the chloride content of aggregate for use in concrete. The use of seawater, chloride-bearing aggregates or admixtures (e.g., $CaCl_2$) *is thus strictly controlled.*

Table 6.3.1 Chloride content classes and maximum chloride content of concrete according to EN 206-1.

Concrete use	**Chloride content class**	**Maximum Cl^- content by mass of cement**
Not containing steel reinforcement or other embedded metal with the exception of corrosion-resisting lifting devices	Cl 1,0	1.0 %
Containing steel reinforcement or other embedded metal	Cl 0,20	0.20 %
	Cl 0,40	0.40 %
Containing prestressing steel reinforcement	Cl 0,10	0.10 %
	Cl 0,20	0.20 %

Chloride penetration is a process which takes place in totally or partly water-filled pores. This is the main reason that as a process is much slower than carbonation, where CO_2 molecule may penetrate faster via air-filled pores. The moisture availability of the environment and the origin of Cl^- were taken into account in the definition of the ***exposure classes in EN 206.*** As in the case of carbonation and corrosion processes, chloride penetration and corrosion require water. In this case, chloride penetration and corrosion are much faster at higher water contents of concrete pores, and consequently at higher moisture contents of the ambient environment [1,10]. 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 environment is presented in Table 6.3.2 [this work; 1,10]. An estimation of the corrosion risk for various relative humidity regions is also presented [this work, 1].

In order to investigate if the EN 206 recommendations for limiting composition values would ensure a service life of 50 years, the above mathematical model was used, and the results are presented in Table 6.3.3. Typical cement types were examined, CEM I 42,5N and CEM II/B-M 32,5N, for concrete production, using common crushed aggregates of maximum size of 31.5 mm. An air content of 3% was assumed.

Table 6.3.2 Exposure classes according to EN 206 for possible corrosion induced by chlorides, correlation with measurable relative humidity (RH) and estimation of chloride penetration and corrosion risks.*

Class	Description of the environment	Informative examples	RH (%)	Cl^- risk	Corr. risk
No risk of corrosion or attack					
X0	For concrete with reinforcement or embedded metal: Very dry	Concrete inside buildings with very low air humidity	<45	0	0
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	< 80	1	2
XS2	Permanently submerged	Parts of marine structure	> 98	3	1
XS3	Tidal, splash and spray zones	Parts of marine structure	> 80	3	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:					
XD1	Moderate humidity	Concrete surfaces exposed to airborne chlorides	< 80	1	2
XD2	Wet, rarely dry	Swimming pools, concrete exposed to industrial waters containing chlorides	> 98	3	1
XD3	Cyclic wet and dry	Parts of bridges exposed to spray containing chlorides, pavements, car park slabs	> 80	3	3

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

In the case of concrete containing reinforcement and subjected to contact with **chlorides from sea water**, for all exposure classes: **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), the recommendations of EN 206 ensure a service life greater than 50 years (even 100 years); for an adequate cover, see Table 6.3.3. We suppose a non-protected concrete surface, exposed to Atlantic Ocean environment (Cl^- concentration: 20 kg/m^3). It has to be emphasized that on the contrary to the carbonation results, cement types that contain supplementary cementing materials (SCM: silica fume, fly ash, etc.) exhibit significantly longer initiation period than the pure portland cement.

Table 6.3.3 Estimated lower bound of concrete service life for various cement types and exposure classes, in the case of chloride-induced corrosion of reinforcement.

COMPOSITIONAL AND DESIGN CHARACTER.	XS1	XS2	XS3	XD1	XD2	XD3
Cement type CEM I 42.5N						
Maximum ratio W/C	0.50	0.45	0.45	0.55	0.55	0.45
Minimum content C (kg/m^3)	300	320	340	300	300	320
Minimum strength class	C30/37	C35/45	C35/45	C30/37	C30/37	C35/45
$t_{cr,chlor}$ (years) for c = 30 mm	63	25	32	43	8	32
$t_{cr,chlor}$ (years) for c = 35 mm	80	35	46	57	12	43
$t_{cr,chlor}$ (years) for c = 40 mm	100	48	58	72	16	53
$t_{cr,chlor}$ (years) for c = 45 mm	>100	58	70	90	20	64
$t_{cr,chlor}$ (years) for c = 50 mm	>100	69	81	>100	24	77
Cement type CEM II/B-M(W-P-LL) 32.5N						
Maximum ratio W/C	0.50	0.45	0.45	0.55	0.55	0.45
Minimum content C (kg/m^3)	300	320	340	300	300	320
Minimum strength class	C25/30	C30/37	C30/37	C25/30	C25/30	C30/37
$t_{cr,chlor}$ (years) for c = 30 mm	70	38	35	54	15	46
$t_{cr,chlor}$ (years) for c = 35 mm	100	50	48	78	20	59
$t_{cr,chlor}$ (years) for c = 40 mm	>100	67	60	>100	28	78
$t_{cr,chlor}$ (years) for c = 45 mm	>100	84	75	>100	37	>100
$t_{cr,chlor}$ (years) for c = 50 mm	>100	100	95	>100	46	>100

W/C: water to cement ratio by weight, C: cement content in concrete (kg/m^3), c: concrete cover to reinforcement (mm), $t_{cr,chlor}$: initiation period for chloride-induced corrosion of reinforcement.

In the case of concrete with reinforcement and subjected to contact with **water containing chlorides including de-icing salts**, from sources other than from sea water, for all exposure classes: **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), the recommendations of EN 206 ensure a service life greater than 50 years (in some cases even 100 years); for an adequate cover, see Table 6.3.3. Especially for XD2, in spite of the low initiation period, the total life is much longer due to prolonged propagation period; however, a denser design may be required. We suppose a non-protected concrete surface, exposed to a Cl^- concentration of 100 kg/m^3, lasting for 1/5 of the year. In this case also blended cements with SCM, or when an SCM is added separately to the concrete mixture, the estimated initiation period is greater than in the case of pure portland cement use.

6.4 Protection measures

6.4.1 Protection against corrosion

Although many recommendations for concrete cover and quality aimed at extending the initiation period in corrosion ($t_{cr,chlor}$) as far as possible, there are circumstances in which it is impossible to prevent corrosion being initiated. Much research has therefore been carried out to determine the factors that control *the corrosion rate at the propagation period.* Some of the most important conclusions are summarized in the following [44]:

1. *The spacing and relative size of the anode and cathode in the corrosion cell.* Relatively porous areas of a concrete member will allow rapid penetration of chlorides, depassivating a small area of steel to form the anode. The remainder reinforcement forms a large cathode area, resulting in a concentration of the corrosion current, and hence a high corrosion rate, at he anode.
2. *The availability of oxygen and moisture, particularly to sustain the cathodic reaction.* If the supply of either is reduced, then the corrosion rate is reduced. Hence little corrosion occurs in completely dry concrete, and little also in permanently saturated concrete, through which O_2 diffusion is difficult.

3. *The electrical resistivity of the electrolyte of the corrosion cell, i.e., the concrete.* By increasing moisture content, chloride content and porosity, the resistivity of concrete is reduced, and hence the corrosion rate is increased. The use of SCM either as cement constituents or as concrete additions can also reduce dramatically the chloride penetration and further the corrosion rate.

In the circumstances when protection against corrosion cannot guaranteed by selection of the materials and proportions of the concrete, depth of cover and attention to sound construction practice, one or more of the following **extra protective measures** may then be taken [1,44, 114]:

- The addition of a *corrosion inhibiting admixture*, such as calcium nitrite, to the fresh concrete.
- The use of *corrosion-resistant stainless steel* reinforcing bars, or *epoxy-coated* conventional bars.
- *Cathodic protection of the reinforcement*, i.e., applying a voltage from an external source sufficient to ensure that all of the steel remains permanently cathodic.
- Applying a *protective coating or an impregnation technique to the concrete*, to reduce chloride, moisture and/or oxygen ingress.

6.4.2 Protection by using waterproof sealants

Let us suppose the case of exposure in an *aggressive environment* (presence of seawater or de-icing salts). Let us suppose also that in some parts of the structure, a *failure* in the designed cover occurred or a cover less than the recommended one was selected, due to technical or economical reasons. If the same service life is required, then the concrete surface should be covered by a protective coating (i.e., an *asphalt membrane*) to maintain the same lifetime. However, this coating can be considered as waterproof only for some years, say *X*. Then, the chlorides can easily attack the concrete through coating holes for some years, say *Y*. Then, a repair takes place which will protect the concrete for X years, and the cycle again starts. Let us suppose that the number of repairs is *n* within the designed service lifetime, Z, (a small number of 2-5 should be expected). Thus:

$$Z = n\,(X + Y) \tag{6.4.1}$$

$$\rho = Y / (X + Y) \tag{6.4.2}$$

where, *ρ* is the *exposure ratio* (see on 6.2.2 section). As mentioned, the free chloride concentration at any time and distance is independent of the number of repairs, *n,* and it can be calculated by multiplying that of the continuous exposure by the exposure ratio, ρ. Thus, the free chloride concentration at the designed service lifetime, Z, at any distance from the concrete surface, is given by:

$$\varepsilon\,[\mathrm{Cl}^-(aq)]_{\rho,Z} = \rho\,\varepsilon\,[\mathrm{Cl}^-(aq)]_{\rho=1,\,Z} \quad \text{(denoted as } \mu) \tag{6.4.3}$$

In order to ensure reinforcing bar protection at a given cover c, the following requirement should be fulfilled:

$$\mu + \frac{K_{eq}\mu}{\varepsilon + K_{eq}\mu}\left[\mathrm{Cl}^-(\mathrm{s})\right]_{\mathrm{sat}} \leq \left[Cl^-(total)\right]_{cr} \tag{6.4.4}$$

Having calculated the free chloride concentration for the case of continuous exposure (ρ=1) at the design service lifetime of Z years, the dependence of concrete cover on exposure degree can be estimated, see an example in [31]: As the problem is independent of the number of repairs, any n can be selected, say n=5, thus in a design service lifetime of 100 years, the coating shall be repaired every 20 years. Let us suppose that the mean concrete cover in a part of the structure is 30 mm. According to [31] example, a maximum exposure degree of ρ=0.3 is calculated. This means that the coating shall be completely waterproof for at least (1-0.3).20= 14 years within the 20-year period. If n=2 is selected, then the coating shall be waterproof for 35 years in a 50-year period.

7. COST CALCULATION AND DESIGN OPTIMIZATION

7.1 Concrete production cost

As a common basis, the volume unit of 1 m^3 of fresh concrete will be considered. *The total production cost* of this volume unit, KT (€/m^3), from the materials purchase until concrete delivery, can be analyzed into the following terms:

$$KT = K_P + K_M + K_B + K_G \qquad (7.1.1)$$

where:

K_P: *purchase cost* of materials, €/m^3

K_M: *mixing cost* for concrete production, €/m^3

K_B: cost of concrete *transportation and delivery*, €/m^3

K_G: *other fixed and operational costs*, €/m^3. They include the fixed cost of purchase and establishment of equipment (depreciation values), labor and administration costs and general operational costs.

7.1.1 Purchase cost

The cost that represents the value of the raw materials (including transportation to the plant premises) can be estimated as follows:

$$K_P = C\,U_C + S\,U_S + F\,U_F + A\,U_A + W\,U_W + D\,U_D \qquad (7.1.2)$$

where:

U_C: cement value, €/kg

U_S: silica fume value, €/kg

U_F: fly ash value, €/kg

U_A: aggregate value, €/kg

U_W: water value, €/kg

U_D: total admixture value, €/kg

7.1.2 *Mixing cost*

The cost of material mixing and preparation of the fresh concrete, K_M, can be estimated by:

$$K_M = P_M \; t_M \, U_E \qquad (7.1.3)$$

where:

P_M: mixing power / m^3 of concrete, J/s.m^3,

U_E: cost of energy, €/J

t_M: the mixing time, s

Parameters P_M and t_M depend on concrete workability and density and, therefore, on concrete composition parameters (CCP: C, S, F, A, W and D).

7.1.3 *Transportation and delivery cost*

The cost of transportation, K_T, primarily depends on the distance between project location and plant, and consequently is independent of concrete compositional parameters. At the project location, the cost is burdened with pumping and application expenses and thus the total cost can be estimated by:

$$K_B = K_T + (P_B / Q) \, U_E \qquad (7.1.4)$$

where:

P_B: pumping power, J/s

Q: concrete flow, m^3/s

Parameter P_B depends on concrete compositional parameters, through workability and density.

7.2 Mix design optimization

The most important *properties* regarding concrete production are three: strength, durability and cost (dependent variables). All of them are functions of the *concrete compositional parameters* (*CCP*: independent variables, primarily C, P, A, W and D contents).

The strength, f_c, in general, is a function of CCP, time (t) and curing conditions, i.e.:

$$f_c = f_c \{CCP, curing, t\} \tag{7.2.1}$$

From the beginning of 20th century, many efforts have been made to approach this dependence by analytical expressions based on concepts of porosity, degree of hydration, etc. (e.g., Abrams' law, Feret and Bolomeys' relationships, etc., see chapter 4. At a specified time, strength depends mainly on W/C ratio, cement content and standard strength class, additions activity and content, quality of aggregates, air-content, and the curing procedure. The Eqs. (4.2.5) or (4.3.1) can be applied as a first approximation.

The durability, expressed as service lifetime of structure, Z, is also a function of CCP, curing conditions, concrete cover, and environmental conditions (deterioration mechanism):

$$Z = Z \{CCP, curing, concrete\ cover, environmental\ conditions\} \tag{7.2.2}$$

For carbonation and chloride-induced deterioration mechanisms, the lifetime can be predicted accurately, using the relationships given in chapters 5 and 6, respectively.

The total production cost, KT, depends on CCP and other parameters (see, section 7.1.1):

$$KT = (C\ U_C + S\ U_S + F\ U_F + A\ U_A + W\ U_W + D\ U_D) + K_M + K_B + K_G \tag{7.2.3}$$

To the above equations, the *mass balance equation* must be added:

$$C/d_C + S/d_S + F/d_F + A/d_A + W/d_W + D/d_D + \varepsilon_{air} = 1 \quad (7.2.4)$$

Thus, for a total optimization these relationships (7.2.1)-(7.2.4) have to be taken into account. The following conditions must also be fulfilled:

$$CH \geq 0, \quad W \geq H \quad (7.2.5)$$

In other words, the SCM content must not exceed P_{max} in order sufficient calcium hydroxide to exist for completion of pozzolanic activity, and the W content must not be lower than the minimum required water (H) for completion of both hydration and pozzolanic activity, see chapter 3.

An **optimization strategy** could be as follows:

Optimization target: Determination of the optimum CCP values that give a minimum cost (KT_{min}), for a required strength (f_c*) and service lifetime (Z*).

Parameters for optimization: n (e.g., C, S, F, A, W, etc.)

Equations: f_c*= f_c {CCP, for given curing and time)
Z*= Z {CCP, for given curing, cover and environment}
Eq. (7.2.4)
Fulfillment of Eq. (7.2.5)

Using the above equations, all n-1 parameters may be expressed as a function of one parameter, say cement content, C (as the most fundamental of all concrete properties). Thus, the optimum value for this parameter can be calculated from the following equation:

$$\partial KT / \partial C = 0 \Rightarrow$$
$$U_C + U_S \partial S/\partial C + U_F \partial F/\partial C + U_A \partial A/\partial C + U_W \partial W/\partial C + U_D \partial D/\partial C = 0$$
$$\Rightarrow C_{opt} \text{ and then } CCP_{opt}.$$

and then knowing the dependence of the other n-1 parameters on C, their optimum values can be estimated. If the dependence is not known, iteration methods of optimization may be followed.

Notation

Latin Letters

A	aggregate-content in concrete volume (kg/m^3)
A/C	aggregate-to-cement ratio, by weight
AI	activity index of SCM (%)
b	parameter in Feret's formula
b_1 , b_2	parameters in Abrams' formula
c	concrete cover: distance of reinforcement from the outer surface of concrete (m)
C	initial cement-content in concrete volume (kg/m^3)
C_{eq}	total equivalent cement-content in concrete (kg/m^3)
CAFH	C_6AFH_{12} content in concrete (kg/m^3)
CAH	C_4AH_{13} content in concrete (kg/m^3)
$CA\bar{S}H$	$C_4A\bar{S}H_{12}$ content in concrete (kg/m^3)
CH	calcium hydroxide content in concrete volume (kg/m^3)
$[Cl^-(aq)]$	concentration of Cl^- in the aqueous phase of concrete (kg/m^3 pore solution)
$[Cl^-(s)]$	concentration of Cl^- in the solid phase of concrete (kg/m^3 concrete)
$[Cl^-(s)]_{sat}$	saturation concentration of Cl^- in the solid phase (kg/m^3 concrete)
CO_2	carbon dioxide content in the ambient air at the concrete surface (%)
$[CO_2]$	carbon dioxide concentration in the gaseous phase of concrete (kg/m^3 pore)
CS	calcium sulphate content in concrete (kg/m^3 of concrete)
CSH	calcium silicate hydrate content in concrete volume (kg/m^3)
d	thickness of mortar coating (m)
d_A	aggregate density (kg/m^3)
d_C	cement density (kg/m^3)
d_{CON}	fresh concrete density (kg/m^3)
d_D	admixture (solids) density (kg/m^3)
d_F	fly ash density (kg/m^3)
d_L	lime density (kg/m^3)
d_{MOR}	fresh mortar density (kg/m^3)
d_S	silica fume density (kg/m^3)

d_W	water density (kg/m^3)
D	total admixture-content (solids) in concrete volume (kg/m^3)
D_{e,Cl^-}	intrinsic effective diffusivity of Cl^- in concrete (m^2/s)
$D_{e,CO2}$	effective diffusivity of CO_2 in carbonated concrete (m^2/s)
D_{max}	maximum nominal upper aggregate size
E	activation energy (J/gmol)
f_c	compressive strength of concrete (MPa)
$f_{c,cube}$	compressive strength of concrete determined by testing cubes (MPa)
$f_{c,cyl}$	compressive strength of concrete determined by testing cylinders (MPa)
f_{ci}	individual test result for compressive strength of concrete (MPa)
$f_{ck,cube}$	characteristic compressive strength of concrete determined by testing cubes (MPa)
$f_{ck,cyl}$	characteristic compressive strength of concrete determined by testing cylinders (MPa)
f_{cm}	mean compressive strength of concrete (MPa)
$f_{i,K}$	weight fraction of constituent i (i=C, Cf, S, A, F, $\overline{S}$, R) in portland clinker
$f_{i,P}$	weight fraction of constituent i in SCM
$F_{h,i}$	degree of hydration of portland clinker phase i
$F_{p,j}$	degree of pozzolanic reaction of SCM-oxide j
F	initial fly ash-content in concrete volume (kg/m^3)
H	chemically-bound water content in concrete volume (kg/m^3)
k	efficiency factor of SCM comparing to portland cement
K	clinker content in concrete (kg/m^3 of concrete)
KT	total production cost of concrete (€/m^3)
K_B	cost of concrete transportation and delivery (€/m^3)
K_{eq}	equilibrium constant for Cl^- binding (m^3 of pore solution/kg)
K_G	other fixed and general costs in concrete production (€/m^3)
K_M	mixing cost for concrete production (€/m^3)
K_P	purchase cost of materials for concrete production (€/m^3)
K_T	cost of concrete transportation (€/m^3)
L	lime content in mortar volume (kg/m^3)
L/C	lime-to-cement ratio, by weight
M	distance between outer surface and axis of symmetry (m)
MAC	mac content in concrete (kg/m^3 of concrete)
n	number of repairs of the protective coating in the total designed lifetime

p_1 , p_2	parameters in Bolomey's formula
p_{CS}	percentage of calcium sulphate in the cement (%)
p_K	percentage of clinker in the cement (minus calcium sulphate) (%)
p_{MAC}	percentage of minor additional const. in the cement (minus calcium sulphate) (%)
p_{PO}	percentage of other pozzol. materials in the cement CEM V (minus calc. sulph.) (%)
p_{SCM}	percentage of SCM in the cement (minus calcium sulphate) (%)
p_{SL}	percentage of slag in the cement CEM V (minus calcium sulphate) (%)
P	SCM content in concrete (kg/m^3 of concrete)
P_B	pumping power in concrete application (J/s)
P_M	mixing power in concrete production (J/s.m^3)
q	quantities in algebraic formulae
q_c	rate of corrosion of the steel bar in concrete (10^{-4} g/cm^2/yr)
Q	fresh-concrete flowrate (m^3/s)
Q_{cr}	critical amount of corrosion that causes splitting of the cover (10^{-4} g/cm^2)
r	degree of pozzolanic reaction of both slag and pozzolan in type CEM V cement
$r_{h,i}$	hydration rate of the portland clinker phase i (mol/m^3.s)
$r_{p,j}$	pozzolanic reaction rate of SCM-oxide j (mol/m^3.s)
R	gas universal constant (8.314 J/gmol.K)
R	rest constituents' content in concrete (kg/m^3)
RH	ambient relative humidity (%)
S	initial silica fume-content in concrete volume (kg/m^3)
SL	slag content in concrete (kg/m^3 of concrete)
SS	standard strength class of cement: compressive strength at 28 days (MPa)
t	time (s)
t_a	time of application of mortar coating (s)
$t_{cr,carb}$	critical time required for reinforcement depassivation due to carbonation (s)
$t_{cr,chlor}$	critical time required for reinforcement depassivation due to Cl^- penetration (s)
t_d	time required for total carbonation of mortar coating (s)
$t_{pr,carb}$	critical time required for carbonation-induced corrosion to split the cover (years)
t_M	mixing time in concrete production (s)
T	period of the complete exposure-nonexposure cycle (years)
U	value of concrete constituent C, SCM, A, W, or D per unit (€/kg)
U_E	cost of energy (€/J, note: $2.773.10^{-7}$ kWh/J)

W	initial water-content (effective) in concrete volume (kg/m^3)
W/C	water-to-cement ratio, by weight
x	distance from the outer surface of concrete (m)
x_c	concrete carbonation depth measured from concrete surface (m)
$x_{c,a}$	intitial (without any coating) carbonation depth of concrete (m)
X_c	carbonation depth measured from coating outer surface (m)
Z	designed service life of a concrete structure (years)
Z_{carb}	designed service life of a concrete structure regarding carbonation (years)

Greek Letters

$\gamma_{i,P}$	weight fraction of oxide i in SCM, which contributes to the pozzolanic reactions
$\Delta\varepsilon_c$	porosity reduction due to carbonation
$\Delta\varepsilon_h$	porosity reduction due to hydration of portland cement
$\Delta\varepsilon_p$	porosity reduction due to pozzolanic activity
$\Delta\overline{V}_j$	molar volume difference between solid products and reactants in j reaction (m^3/kg)
ε	total concrete porosity (m^3 pore volume /m^3 concrete)
ε_0	porosity of fresh concrete
ε_{air}	volume of entrained or entrapped air per concrete volume (m^3/m^3)
ε_C	porosity of carbonated concrete
ε_{eff}	effective porosity of concrete regarding chloride diffusion
λ	correction factor of carbonation depth for RH<55%
ρ	ratio of the exposure time to the total time of a complete cycle

Subscripts

0	quantities referring to x=0
A	quantities referring to aggregates
ACT	maximum part of SCM that may participate in the pozzolanic reactions
carb	quantities reffering to concrete carbonation
cr	critical quantities for steel depassivation
D	quantities referring to chemical admixtures
F	quantities referring to fly ash
i	oxide C, Cf, S, A, F, $\overline{S}$ or R (see cement techn. not.; Cf: free CaO, R: other const.)
in	quantities referring to t=0

j	age in days
K	quantities referring to portland clinker
opt	quantities calculated from an optimization technique
P	quantities referring to SCM
S	quantities referring to silica fume
W	quantities referring to water

Superscripts

*	required quantities
(1)	quantities referring to cement-lime mortar coating
(2)	quantities referring to concrete

Abbreviations

AASHTO	American Association of States Highway and Transportation Officials
ACI	American Concrete Institute
AFM	atomic force microscopy
ASTM	American Society for Testing and Materials
BET	Brunauer, Emmett and Teller (method of)
CCP	concrete compositional parameters
C…/…	compressive strength classes in case of normal-weight and heavy-weight concrete
CAL	calcareous
CEB	Comité Euro-international du Béton
CEM…	cement type according to the series EN 197
CEN	Comité Européen de Normalisation
CH	calcium hydroxide
CSH	calcium silicate hydrate
EN	European Standard
mac	minor additional constituent
OPC	ordinary (normal) portland cement
RH	relative humidity
RILEM	Réunion Intern. des Laborat. d’Essais et de Recherches sur les Mat. et les Constr.
SCM	supplementary cementing materials
SEM	scanning electron microscopy

SIL	siliceous
SRPC	sulphate-resistant portland cement
X0	exposure class for no risk of corrosion or attack
XC…	exposure classes for risk of corrosion induced by carbonation
XD…	exposure classes for risk of corrosion induced by Cl^- other than from sea water
XS…	exposure classes for risk of corrosion induced by Cl^- from sea water
XF…	exposure classes for freeze/thaw attack
XA…	exposure classes chemical attack

Cement Technology Notation

S:	SiO_2
A:	Al_2O_3
F:	Fe_2O_3
C:	CaO
M:	MgO
H:	H_2O
$\bar{S}$:	SO_3
$\bar{C}$:	CO_2
LOI:	loss on ignition

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APPENDIX A:
EXPERIMENTAL PROCEDURE FOR ESTIMATION OF CHLORIDE PENETRATION PARAMETERS

A.1 Estimation of chloride binding parameters: K_{eq} and $[Cl^-(s)]_{sat}$

The rate of chloride binding in concrete can be described by the following equation:

$$r = k_a [Cl^-(aq)] ([Cl^-(s)]_{sat} - [Cl^-(s)]) - k_a [Cl^-(s)] / K_{eq} \tag{A.1}$$

At steady-state (equilibrium) the rate vanishes, resulting in the following (inversely linear) relation between the steady-state concentrations:

$$\boxed{\frac{1}{[Cl^-(s)]_\infty} = \frac{1}{[Cl^-(s)]_{sat}} + \frac{1}{K_{eq}[Cl^-(s)]_{sat}} \frac{1}{[Cl^-(aq)]_\infty}} \tag{A.2}$$

Eq. (A.2) allows experimental determination of the parameters K_{eq} and $[Cl^-(s)]_{sat}$, through linear regression on measurements of pairs of values of steady-state concentrations $[Cl^-(aq)]_\infty$ and $[Cl^-(s)]_\infty$ taken on the same material for different initial chloride concentrations, as follows:

1. Sample Preparation: The specimens can be pastes (recommended), mortar, or concrete, cured at least for 3 months in saturated lime water (20°C). After the curing period, they placed into an oven at 105 °C until complete drying (checking by weight stabilization). A representative part from each different specimen is coarsely crushed and all the material is ground to provide samples with particle size less than 2 mm (but not much lower than 0.2 mm). During the preparation, carbonation and overheating should be avoided. The powders are homogenized and can be kept in an oven at 105 °C until testing.

2. Test Procedure: Sodium chloride (NaCl) solutions with chloride concentrations of 0.05, 0.2, 1, and 5 mole/litre are prepared (e.g., 1.46, 5.84, 29.22, and 146.11 g NaCl, respectively placed in 500-ml glass volumetric flasks and filled by water up to the indication). A representative quantity of 10 g of the sample is put in a glass container and filled with 15 ml of NaCl solution. Thus, at least 4 combinations are prepared for each sample. However, additional chloride concentrations may be used extending the experimental accuracy. The containers are sealed and stored at 20 °C for two weeks to reach binding equilibrium. From time to time, and especially during the first 24h, the containers should be well-shaken ensuring satisfactory mixing.

3. Chloride Analysis: A quantity of 2-5 g solution is received from the containers by filtration. The chloride concentration in the solution can be determined by the Volhard titration method in accordance with the Nordic standard NT Build 208 (1984), and it is expressed as % Cl^- by weight of solution.

4. Calculations: The steady-state concentrations $[Cl^-(aq)]_\infty$ and $[Cl^-(s)]_\infty$ are calculated as:

$$[Cl^-(aq)]_\infty = \frac{\chi}{100}\rho_{sol} \qquad \text{:\underline{free chlorides}} \qquad (A.3)$$

$$[Cl^-(s)]_\infty = \left(\left[Cl^-(aq)\right]_0 - \frac{\chi}{100-\chi}\delta_{sol} \right) \frac{V_{sol}\rho_s}{m_s} \qquad \text{:\underline{bound chlorides}} \qquad (A.4)$$

where, χ: % Cl^- by weight of solution (i.e., χ kg Cl^- /100 kg solution; measured), ρ_{sol}: density of the solution (kg/m^3 solution; given in reference 38), $[Cl^-(aq)]_0$: initial chloride concentration in the solution (kg/m^3 solution; given in Table A.1), δ_{sol}: initial water content of the solution (kg H_2O/m^3 solution; given in Table A.1), V_{sol}: volume of the solution (15.10^{-6} m^3), m_s: sample mass (10.10^{-3} kg), and ρ_s: density of the initial paste or mortar specimen at a dry condition (it has to be determined; about 2200 kg/m^3).

5. Parameter Estimation: Through linear regression of $1/[Cl^-(s)]_\infty$ (y) versus $1/[Cl^-(aq)]_\infty$ (x) results, the parameters are estimated from the slope and intercept as follows:

$$y = a\,x + b, \qquad [Cl^-(s)]_{sat} = 1/b, \qquad K_{eq} = b/a \qquad (A.5)$$

Table A.1 Parameter values for calculations*.

Chloride Solution, (mole/litre)	**$[Cl^-(aq)]_0$ ($kgCl^-/m^3$ solution)**	**δ_{sol} (kg H_2O/m^3 solution)**
0.05	1.775	997.4
0.2	7.1	994.8
1	35.5	980.1
5	177.5	893.6

*These values, as well any others for different initial chloride concentrations can be found in Reference 38.

A.2 Determination of intrinsic chloride diffusivity, D_{e,Cl^-}

1. Test Procedure: Long-term ponding experiments have to be performed, according to nordtest method NT Build 443 (1995). Prior to the immersion in the chloride solution, the samples (concrete or mortar cylinders or prisms) are coated by epoxy resin and then a slice of 10 mm thick from one end is removed. The samples are immersed in a chloride solution (165g NaCl/l solution) for at least 100 days (t_{max}). The temperature is kept constant at 20°C throughout the entire test period. At the end of the immersion period, the exposed surface is ground using a dry process in a diameter of 75 mm receiving thin successive layers from different depths (i.e., 1-2, 3-4, 5-6, 8-10, 12-15, 18-21, and 21-24 mm from the external surface) and yielding the chloride profile at that particular time. The total chloride content of the powders is determined by the Volhard titration method in accordance with the Nordic standard NT Build 208 (1984), and it is expressed as % Cl^- by weight of dry concrete (or mortar).

2. Calculations: The total chloride concentration $[Cl^-(t)]$ is calculated as follows (in kg/m^3 concrete):

$$[Cl^-(t)] = \frac{\chi\rho_S}{100-\chi} \qquad \text{:total chlorides} \qquad (A.6)$$

where, χ: % Cl^- by weight of dry concrete (i.e., χ kg Cl^- /100 kg dry concrete; measured), and ρ_s: density of the initial concrete or mortar specimen at a dry condition (it has to be determined; about 2200 kg/m^3).

3. Diffusivity Estimation: Solving Eq. (6.2.1)-(6.2.4) for the parameter values of this case, i.e.,

K_{eq} and $[Cl^-(s)]_{sat}$: determined as previously or calculated by Eq. (6.2.8) and (6.2.9),
ε: measured or calculated by Eq. (3.2.17), (3.2.28), (3.2.35) or (3.2.43)
$[Cl^-(aq)]_0$= 100 kg/m^3,
M: specimen length, t_{max}=100 days,
time-step: 60-600 sec, cells in space N: 100 (i.e., space-step: M/N),

and using an initial value for D_{e,Cl^-} estimated approximately by Eq. (6.2.5) and (6.2.6), the total concentration of chlorides (i.e., $[Cl^-(t)]=\varepsilon[Cl^-(aq)]+[Cl^-(s)]$) is calculated. For the solution of these equations, the program EUCON should be used (see *user's manual*). The calculated profile is compared with the experimental values, and a new diffusivity value is taken to improve fitting. This procedure is repeated until satisfactory fitting of the model predictions to the experimental results, yielding an *optimum value* for the intrinsic diffusivity parameter (a least-square optimization technique may be used).