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Causes and mechanisms of deterioration in reinforced concrete

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Abstract: The physically and chemically induced deterioration causes and mechanisms of reinforced concrete structures are discussed. Physically - induced deterioration is caused by freeze–thaw loads, non-uniform volume changes, temperature gradients, abrasion, erosion, or cavitation. Chemically-induced deterioration consists of carbonation, corrosion of steel reinforcement, sulfate and acid attacks, or alkali–aggregate reactions. The role of moisture and microstructure of different concrete types is also considered.

Key words: deterioration of concrete, microstructure, moisture, reinforcement, physical attacks, chemical attacks.

1.1 Introduction

The overall durability of concrete is relatively good; otherwise it could not have become the most abundantly used building material in the world. Concrete is also a building material whose durability properties can be improved quite easily and in a versatile manner simply by selecting its constituents appropriately or by using proper admixtures. However, these possibilities have not been exercised sufficiently because too often the cheapest possible concrete type has been selected for the structure, despite the demanding environmental conditions to which it will be exposed. Not only have economical considerations during the building phase governed the choice of concrete type, but also lack of knowledge of different deterioration mechanisms and of the ways to improve the durability properties of concrete have been the reasons why the service lifespan of many contemporary concrete structures has been unexpectedly short.

At the global level, the cost of renovating deteriorating concrete structures is huge. It is usually the case that relatively inexpensive measures taken at the design and erection stage could have increased the service lifespan of these structures by a factor of two or even three.

In this chapter, the causes and deterioration mechanisms will be reviewed. The emphasis has been on the most important deterioration features which affect large volumes of concrete structures.

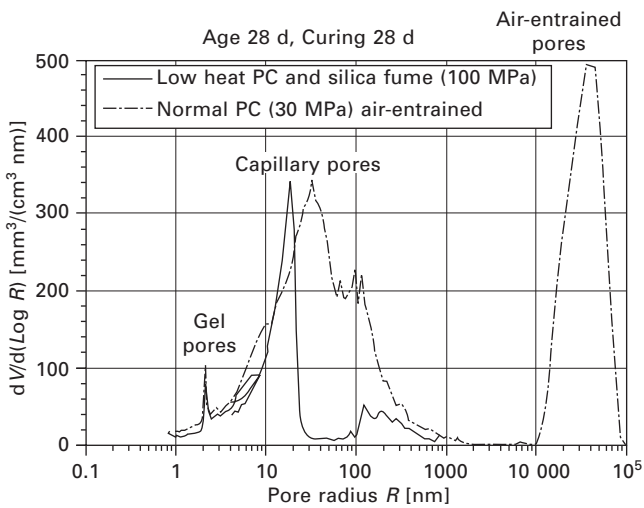
1.2 Microstructure and role of moisture in concrete deterioration

Concrete can be considered as one of the most non-homogeneous and demanding engineering materials used by mankind. This man-made artificial stone consists of aggregates having a wide dimensional range from sub-micron sized particles to several centimeters. Aggregate particles are usually surrounded by a highly porous transition zone, differing from the less porous bulk matrix of hydrated and partially hydrated cement paste. Void dimensions range from nanometer sized gel pores of calcium silicate hydrates to micrometer sized capillary pores and larger pores of several millimeters covering a dimensional range of over six orders of magnitude (Fig. 1.1). The pore system is partially filled with water.

The glue phase of calcium silicate hydrates is also very complicated, comprising amorphous and crystalline phases. One of the general features of concrete is the large number of cracks that are induced into it in normal climatic conditions. These defects are partly due to shrinkage tensions caused by the contraction of matrix gel and by moisture and temperature gradients between different parts of the concrete structure.

1.2.1 Effects of water–binder ratio and different binders

Almost all the durability problems of concrete are related to the pore size distribution of binder paste and to the degree of filling of pores by liquid.



1.1 Pore size distribution of binder pastes. Gel pores are measured by nitrogen adsorption, capillary pores by mercury intrusion porosimeter, and air-entrained pores from thin section data.

These features affect the pore water transport and subsequent pressures generated into the concrete matrix (concrete skeleton). How the deleterious substances can penetrate into concrete is mainly governed by the dimensions of the entrances between larger capillary pores and by the air-filled portion in the pore system. Cracks on the outer surface of the concrete structure also increase the penetration of water and deleterious substances into concrete. When the intruding deleterious substance is in the gaseous phase, diffusion takes place much faster if a considerable part of the pore volume is air-filled.

Depending on the deterioration mechanism, there is usually a relative humidity range measured in the pore system, during which the deterioration mechanism proceeds at an increased rate. For example, the carbonation rate of concrete is highest at 50–70% relative humidity in ambient air.

When the penetrating deleterious substances are in ionic form, the penetration rate depends on the concentration differences in pore water between the surface and interior concrete. Also, pressure difference between the different parts of the structure can act as the driving force which governs the penetration rate of the deleterious substances. In this type of transport mechanism, the dimensions of the entrances between much larger capillary pore voids and the size of the intruding molecules govern the permeability of concrete.

In the case of the diffusion mechanism, Fick's first law is not adequate to model the transport mechanism of concrete, because there is also a counter-diffusion of ions having opposite charge which strongly affects the process. Similarly, in the case of liquid penetration, Darcy's law has been proven to be too simple. The effect of entrance dimensions between capillary pores and the air volume in them cannot be modeled with proper accuracy simply by using the material properties such as water/cement ratio or air content.

Drying and wetting of concrete pore structure has a significant effect on the penetration rate, and this complicates the transport mechanism. Therefore, simple first-order diffusion and transport formulae cannot be applied in analyzing the deterioration rates in concrete. Additionally, the introduction of large air-filled protective pores (dimensions 0.02–0.1mm) by air-entraining admixtures successfully hinders the capillary flow of pore water and, therefore, air-entrainment affects all types of corrosion mechanisms in which deleterious substances intrude inside concrete from the surface of the structure.

If the binder is pure Portland cement, capillary pore volume can be calculated quite accurately as a function of water/cement ratio, hydration degree, and air content of fresh concrete. However, the effects of the entrance dimensions between larger capillary pore voids are not known sufficiently well to calculate the diffusion or permeability coefficients. The effect of additional binders such as condensed silica fume on total capillary porosity can be calculated but, again, knowledge of how it affects the entrance

dimensions is not adequate. The effects of other secondary cementitiuous materials such as fly ashes are known to an even lesser degree.

Hydration of ground granulated blast furnace slag (GGBS) produces in concrete a microstructure which differs remarkably from that when Portland cement alone is used. Hydration of GGBS resembles a surface reaction of the binder particles. If proper curing measures are applied, the permeability of slag concrete is much smaller compared to Portland cement-based concrete when both concrete types are produced with the same water/binder ratio. However, carbonation of slag concretes coarsens the pore structure and, during later ages, permeability of slag concretes is increased (Matala, 1995). Carbonation also increases the permeability of concretes in which secondary cementitious materials have been used. Such pozzolanic materials are condensed silica fume and fly ash. Additional hydration of cracked concrete can sometimes heal the structure if there is moisture available. In regions subject to freeze–thaw deterioration in particular, this healing during summer times can increase the lifespan of the structure.

The variation in diffusion or permeability coefficients in different concretes produced by different cements and secondary cementitious materials is quite large. However, decreasing the water/cement or water/binder ratio and increasing the curing time makes all concretes more impermeable against penetration of deleterious substances and, thus, the estimated lifespan is increased. There exists also large deviation in the estimated lifespan due to different deterioration mechanisms. Therefore, no general rules can be given and different deterioration rates have to be assessed for different corrosion mechanisms.

1.2.2 Pore water transport and pore water tension-induced stress state

The pore system of concrete is seldom saturated by pore water. Therefore, there is a tensional stress state in pore water which causes compression in concrete. The tension in pore water can be calculated by applying Kelvin's equation:

$$p - p_0 = \frac{R \cdot T}{v_w} \cdot \ln \frac{p_v}{p_{v0}} \qquad [1.1]$$

in which R is ideal gas constant 8.314 J/mol/K, T is temperature in K, v_w is specific volume of water in m^3/mol, p_v is vapor pressure of pore water, p_{v0} is the saturation vapor pressure, and p_0 is atmospheric pressure 0.1 MPa.

When concrete begins to dry from the surface, the pore water tension generated causes compression on the surface concrete layer which decreases

the permeability of the surface. However, during cyclic moisture loads, this compression is alleviated and cyclic moisture loads increase moisture transport through the surface layer. Then, the moisture flow is significantly increased compared to the situation when concrete dries without wetting and drying cycles.

During freeze–thaw loads, the transport of water causes considerable pressure differences in the concrete cross-section which can exceed the tensional capacity of concrete. Similarly, cyclic freeze–thaw loads can pump large quantities of external water into concrete, causing increased freeze–thaw stresses.

The inside of concrete also dries due to hydration causing self-desiccation, which generates large pore water tensions inside the structure. Together with shrinkage stresses, these generate cracks into concrete which can increase the transport of deleterious substances into it.

1.3 Physically induced deterioration

Corrosion loads and mechanisms of concrete and reinforcement can be divided into those of external and those of internal origin. External origin mechanisms usually include freeze–thaw deterioration, chloride ingress, carbonation, sulfate attacks, and acid attacks. Effects of alkalis on certain aggregates or deteriorations due to delayed ettringite reaction are included in internal origin mechanism. However, in this chapter the deterioration mechanisms are divided into physically and chemically induced mechanisms according to the main deterioration feature. The initiation of the deterioration mechanism can be caused by a single cause but, thereafter, the deterioration can continue as a combination of several other mechanisms. It can be quite difficult to assess which is the original cause of the initial corrosion.

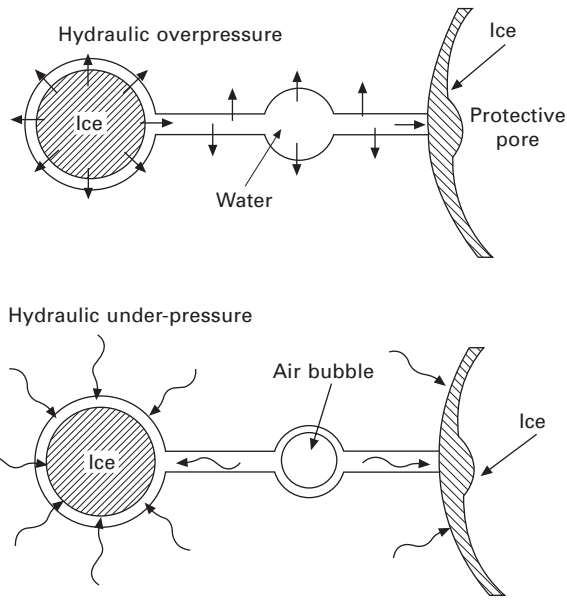
1.3.1 Freeze–thaw deterioration

Two types of deterioration mechanisms are apparent in concrete structures exposed to freeze–thaw loads. In surface scaling, flakes of the outer surface disintegrate and the other mechanism, internal damage, is associated with cracking on the surface or interior of the structure. The causes of these mechanisms are different.

Large surface scaling is observed in concrete structures produced by a high water/cement ratio and low air content when the moisture content in the surface layer is high. The moisture content in the surface layer is high in situations when water is in direct contact with the surface or where there is heavy rain falling on the concrete structure. In these situations, cyclic freeze–thaw loads cause a pumping effect which increases the moisture content and degree of filling of the pore system at the surface to a large

degree. If the air-filled pore volume at the surface is small and the air-filled pores are situated far apart (> 0.4mm), the expansion of about 9%, when water initially freezes, causes hydraulic overpressure in the pore water (Fig. 1.2). This pressure causes disintegration at the surface of the structure, a phenomenon which is related to the concept of critical degree of saturation (Fagerlund, 1977). If the degree of filling of the pore system exceeds the critical degree of saturation, even one freeze–thaw cycle causes deterioration in concrete.

In concrete structures it is usually the case that water content and degree of filling of the pore system are smaller inside the concrete. Therefore, the hydraulic pressure during the initial freezing temperature is smaller and no deterioration takes place. In fact, when there is ice present in the pores of the surface layer, the unfrozen water in the interior of the structure migrates towards the surface layer. This causes a tensional stress state in pore water of the interior portion of the structure. The reason for the water migration is the lower chemical potential of the ice surface compared with the chemical potential of the unfrozen pore water situated in smaller pores inside the structure. This feature also causes micro-ice-lens formation in the pores of concrete, as presented by Setzer (1999, 2001).



1.2 Water pressure mechanisms in freezing concrete. Hydraulic overpressure of pore water at the surface layer of concrete is the main deterioration mechanism in surface scaling while differences of pore water tension (under-pressure) at different locations in the concrete cross-section are responsible for internal damage in freeze–thaw deterioration. (Penttala and Al-Neshawy, 1999)

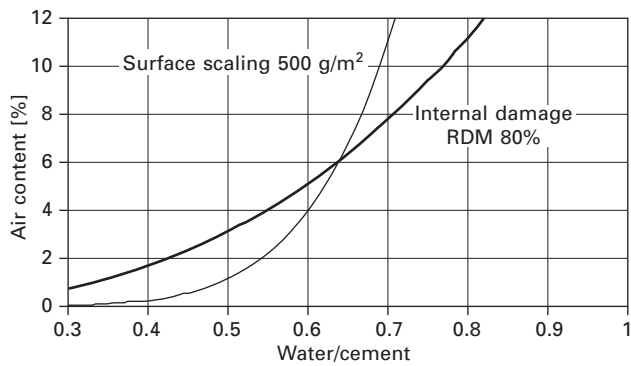
When concrete is produced by using a small water/cement ratio, the capillary pore volume is smaller and the permeability of the surface layer is also decreased, which decreases the moisture content in the surface layer. This reduces the need for air-filled protective pores into which pore water is squeezed by the hydraulic over-pressure, and the water can freeze there without causing surface scaling. Then, the internal damage mechanism becomes the decisive mechanism which governs the need for air-entrainment (Fig. 1.3).

When there is ice in the pore structure of concrete and no additional salts are present in the pore water, pore water tension can be calculated according to Equation [1.2] (Penttala, 1998):

$$p - p_0 = \frac{R \cdot T}{v_i} \ln\left(\frac{p_v}{p_{v0}}\right) + \frac{\Delta h^0_{wi}}{v_i \cdot T_0}(T - T_0) + \frac{1}{v_i} \cdot \int_{T_0}^{T} \int_{T_0}^{T} \frac{c^0_{pw} - c^0_{pi}}{T} \, dT dT \qquad [1.2]$$

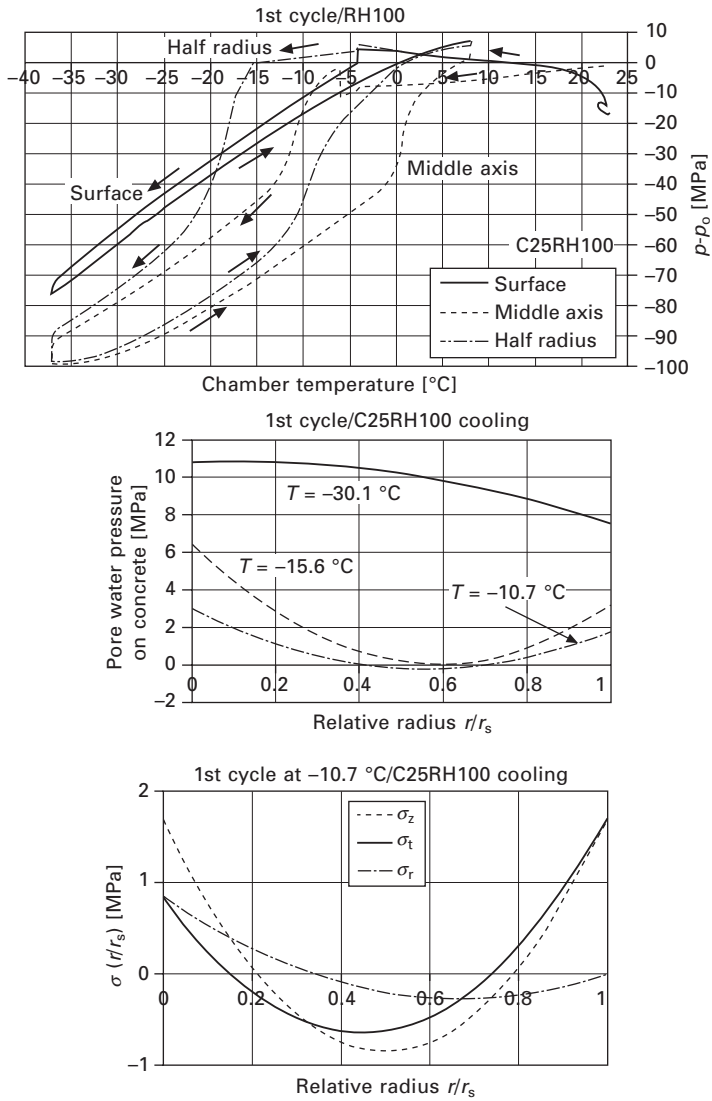
Heat of solidification is $\Delta h^0_{wi} = 6.0 \times 10^3$ J/mol, v_i is specific volume of ice in m^3/mol, and c^0_{pw} and c^0_{pi} are specific heat capacities of water and ice, respectively. The reference temperature T_0 is 273.16 K and the reference pressure p_0 is 0.1 MPa. Pore water tension causes compression in concrete. Air-entrainment causes a higher three-dimensional compressive stress state in concrete compared to non-air-entrained concretes. This hinders crack formation and even closes cracks that have been generated (Penttala, 2007).

In the internal damage mechanism, the pore water tension differences and



1.3 The relation of the needed air-entrainment in the two deterioration mechanisms of concretes as a function of water/cement ratio. Tests are performed by the slab test method (Swedish standard SS13 72 44–1515, 1988) and the curves are calculated by statistical means (Penttala, 2006).

subsequent compression differences in concrete at different locations of the structure cause tensional stresses into concrete. If they exceed the tensional capacity of concrete, cracks are generated (Fig. 1.4).



1.4 Pore water tension as a function of chamber temperature (a). Pore water pressure distributions on concrete (b) and the stress state distributions (c) at the temperature of –10.7 °C as a function of the relative radius of a cylindrical test specimen. The non-air-entrained concrete test cylinder was cured under water and had a compressive strength of 25 MPa (Penttala, 2007).

Air entrainment

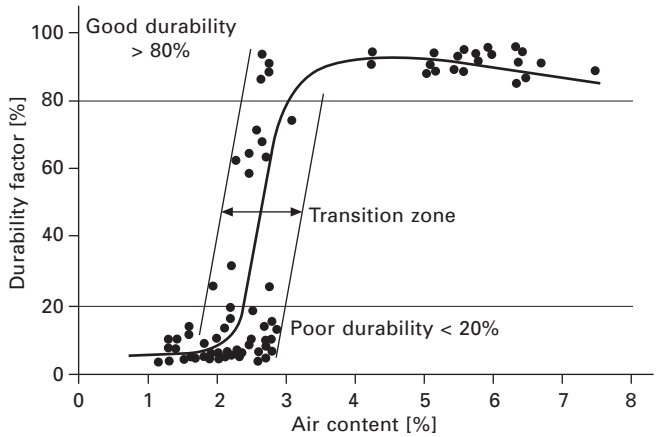
Adequate freeze–thaw durability of concrete can be assessed by increasing the air content in binder paste by air-entraining admixtures. The optimal dimension of these protective air pores ranges from 0.02–0.05 mm. With this size, they stay air-filled in normal moisture load conditions and effectively hinder the capillary flow of pore water in concrete. Also, the strength reduction caused by the pores is still reasonably small.

The air-entraining admixture should be compatible with the concrete composition and with the possible other admixtures used, so that the dispersion of the protective pores in the binder paste is sufficiently homogeneous and the distance from one air-filled pore to the nearest other air-filled pore is sufficiently short (in normal concretes smaller than 0.35–0.45 mm). The spacing factor and the pore size distribution can be assessed by optical means from a thin section test sample cut from hardened concrete, but continuous quality control is usually performed by total air content measurements from fresh concrete by the pressure method.

Normal aggregates are usually durable against freeze–thaw distress and their porosity is rather small. Binder paste is the vulnerable portion of the concrete matrix, and it should possess adequate protective pore size distribution and total air content. Therefore, when freeze–thaw durability in continuous quality control is assessed by air content, the acceptance air content value depends on the relative volume of the binder paste in concrete. The relative binder paste volume is mainly a function of the binder content and maximum aggregate dimension. The water/cement ratio and maximum aggregate dimension are the variables normally used in determining the total air content required in concrete to ensure freeze–thaw durability. If there are no additional salts in the pore water, the air content measured from fresh concrete should exceed 4.5% when the maximum aggregate dimension is 32mm (Fig. 1.5). A sufficient average value can then be 5.5% in which the distribution of the spacing factors of the protective pores has been taken into consideration.

In the estimated service lifespan assessment presented later in the chapter, the sufficient air content value is presented in Table 1.2 as a function of water cement ratio and maximum aggregate size.

The air-entraining admixture dosage required depends on several variables. These include, for example, the coarseness of the cement, quality and type of the secondary cementitious binders, amount of blast furnace slag, fineness and amount of fillers, temperature of concrete, transport distance of fresh concrete, water/cement ratio of the concrete, consistency of the mix, possible pumping of concrete, and other admixtures used in the mix. Depending on the concrete constituents, the air-entraining admixture dosage can be varied and there are national restrictions in the use of some ingredient materials.



1.5 Effect of air-entrainment on the freeze–thaw durability of concrete when the freezing liquid is pure water (Cordon, 1967).

For example, if the carbon content in fly ash is high (> 7%) or changes much between different delivery lots, it is not advisable to use it in the production of freeze–thaw durable concrete.

Effect of salts

If there are salts on the surface of concrete during freeze–thaw loads or if additional salts have intruded into the pore water, the deterioration is significantly more severe compared with normal concretes. Salts increase the surface scaling of the structure, and the deterioration can proceed very rapidly after only few freeze–thaw cycles. This seems to indicate that the main deterioration mechanism in salt-freezing is of physical origin. There are several research results that seem to indicate that a 2–4% salt concentration in the surface water layer causes severe deterioration and, if the salt concentration is higher, the deterioration decreases (Verbeck and Klieger, 1957). However, some salts, especially calcium chloride, in large concentrations and after long exposure, can also cause chemical corrosion in concrete.

When there are salts dissolved into the pore water of concrete, the concentration difference between pore water and external salt-free water or moisture draws more water into the pore system. This increases the freezable water content in concrete considerably and the degree of filling of the pores is increased. Similarly, salts increase the pore water tension in the internal damage mechanism of concrete. The additional dissolved ions in pore water decrease the freezing point, but the degree of filling of the pores of salted concretes is much higher and larger pores are filled with

water compared with unsalted comparison concretes preserved in similar environments. Therefore, the initial freezing temperature of normal concretes and salt-freezing concretes are about the same (Penttala, 1999). Due to super cooling at the initial freezing temperature of the pore water, the freezing ice amount in salted concretes can be several times larger compared with unsalted comparison concrete and, therefore, the hydraulic pressure generated in the surface layer is also much larger. This explains the more severe surface scaling in the salted concretes.

During ice formation, the ice structure is nearly free of salts and the salt concentration increases in the unfrozen pore water. If the initial salt concentration in the pore water is large, the salt concentration in the unfrozen pore water situated in smaller pores can reach the eutectic temperature of the salt combination. When temperature decreases further, salts begin to precipitate, causing large crystallization pressures against the pore walls. This phenomenon causes internal damage in concrete. Similarly, the large concentration differences in unfrozen pore water between the surface layer of the structure and interior concrete into which salts have not been able to intrude cause osmotic pressures in pore water and pore water transport which generate internal stresses in concrete. These mechanisms explain the more severe deterioration of concretes exposed to salts.

At the initial freezing temperature of the pore water, the hydraulic pressure in the surface layer is much higher compared with unsalted concretes. Therefore, the protective pore volume has to be increased and the distance between these air-filled pores has to be decreased. Then the pressured pore water can flow into the protective pores and freeze there without causing damage in the concrete matrix. Similarly, in the salted concretes air-entrainment causes a higher compressive, three-dimensional stress state in concrete compared with non-air-entrained concretes. This hinders crack formation and even closes cracks that have been generated in concrete. The protective pores also alleviate the possible crystallization pressures of the salts.

In the salt-freezing situation, the air content measured from fresh concrete by the pressure method should now exceed about 5.5% when the maximum aggregate dimension is 32mm. The average air content should exceed 6.5%. Similarly, the water/cement ratio should be decreased so that it is below 0.45 in concrete structures exposed to salt freezing loads.

When concrete binder consists of a large amount of GGBS (> 60%) or condensed silica fume (~ 10%), carbonation of the surface layer coarsens the pore structure of these concretes. Due to the coarser pore size distribution, the freezable pore water volume is increased. At salt-freezing loads, the surface layer of these concretes can disintegrate very quickly, after 10–20 freeze-thaw cycles (Matala, 1995).

Estimated service lifespan assessment

In the 2004 Finnish concrete code (CAF, 2004), a calculation method for estimating service lifespan with regard to frost exposure and carbonation is presented. The expected service lifespan can be estimated by equation:

$$t_L = t_{Lr} \cdot A \cdot B \cdot C \cdot D \cdot E \cdot F \cdot G \quad [1.3]$$

where t_L is the estimated service lifespan, t_{Lr} is the reference service lifespan (50 years), and, *A*–*G* are lifespan coefficients reflecting various factors.

Coefficients *A*–*G* in Table 1.1 are different for frost resistance and for carbonation. For example, in frost resistance, coefficient *A* takes into consideration air content, water/cement ratio, and maximum aggregate size. Coefficient *B* depends on massiveness (volume/surface area ratio) of the structure and possible coating of the structure. Coefficient *C* takes into consideration the curing measures. Coefficient *E* depends on the geographical direction and geographical location of the structure and coefficient *G* gives the impact of inspection and maintenance frequency. In carbonation, the effects of concrete strength class, cement type, and air content are taken into consideration in coefficient *A*. Coefficient *B* depends on concrete cover thickness over reinforcement and possible coatings on the concrete surface. Coefficient *C* depends on the curing measures and coefficient E_1 takes into consideration the effects of exposure class, coefficients E_2–E_4 take into consideration geographical direction, geographical location, and frost exposure. Coefficient *G* again depends on inspection and maintenance frequency.

As an example, the estimated service lifespans of concretes situated in environment class XF3 (frost action, horizontal structure, no salt exposure) can be assessed according to Table 1.2. Then only the material-related parameters are taken into consideration and all other coefficients have a value of 1. The estimated lifespan can be calculated by multiplying coefficient *A* by 50 years according to Equation [1.3]. The deterioration formulae by which the coefficient values have been calculated are also presented in the concrete code.

Table 1.1 Factors influencing frost resistance in Finnish concrete code (CAF, 2004)

Coefficient	Factor	Design parameters
A	Materials, porosity	Air content and water/cement ratio
B	Design, structural details	Structure type, coating
C	Performance of work	Curing time
D	Interior climate	–
E	Exterior exposure to weather	Frost exposure class, geographical direction
F	Working load	–
G	Maintenance measures	Inspection and maintenance frequency

Table 1.2 Values of coefficient A in exposure class XF3. Shaded values can be used only in studying the effects of existing structures in the case of poor quality (CAF, 2004)

Air content [%] Max. aggregate size [mm]			Coefficient *A* Effective water/cement ratio								
8	12	> 16	0,3	0,35	0,4	0,45	0,5	0,55	0,6	0,65	0,7
2,5	2,0	1,5	1,04	0,69	0,52	0,43	0,36	0,32	0,29	0,26	0,24
3,0	2,5	2,0	3,12	1,30	0,84	0,63	0,52	0,44	0,38	0,34	0,31
3,5	3,0	2,5	4,00	2,51	1,26	0,86	0,66	0,55	0,47	0,41	0,37
4,0	3,5	3,0	4,00	4,00	1,91	1,14	0,83	0,66	0,55	0,47	0,42
4,5	4,0	3,5	4,00	4,00	3,08	1,50	1,01	0,77	0,63	0,54	0,47
5,0	4,5	4,0	4,00	4,00	4,00	2,00	1,23	0,90	0,72	0,60	0,52
5,5	5,0	4,5	4,00	4,00	4,00	2,77	1,50	1,04	0,81	0,67	0,57
6,0	5,5	5,0	4,00	4,00	4,00	4,00	1,84	1,21	0,91	0,74	0,62
6,5	6,0	5,5	4,00	4,00	4,00	4,00	2,28	1,39	1,02	0,81	0,67
7,0	6,5	6,0	4,00	4,00	4,00	4,00	2,91	1,61	1,13	0,88	0,73
7,5	7,0	6,5	4,00	4,00	4,00	4,00	3,85	1,88	1,26	0,96	0,78
8,0	7,5	7,0	4,00	4,00	4,00	4,00	4,00	2,21	1,41	1,05	0,84
8,5	8,0	7,5	4,00	4,00	4,00	4,00	4,00	2,62	1,58	1,14	0,90
9,0	8,5	8,0	4,00	4,00	4,00	4,00	4,00	3,16	1,77	1,24	0,97
9,5	9,0	8,5	4,00	4,00	4,00	4,00	4,00	3,91	1,99	1,35	1,03
10,0	9,5	9,0	4,00	4,00	4,00	4,00	4,00	4,00	2,25	1,47	1,11

1.3.2 Non-uniform volume changes and temperature gradients

This section studies the effects of phenomena which cause cracking in concrete. Cracks on the concrete surface and around large aggregate particles can drastically increase the permeability of concrete. Cracks form a route for deleterious substances to penetrate into concrete, and this decreases the service lifespan of the structure. Cracks caused due to inadequate reinforcement against mechanical loads and cracking caused by fire loads are excluded from the discussion.

Cracks can be generated in concrete at early ages, during the first days or weeks, due to hydration or production technology-related reasons. At later ages, the non-uniform volume changes are mainly caused by chemically induced reasons such as reinforcement corrosion, carbonation, and alkali-aggregate reactions which will be dealt with in Section 1.4.

Concrete in the fresh state

Depending on the consistency of concrete, segregation of concrete constituents can take place. Heavier aggregate particles segregate to the bottom part of

the mold or form and water rises up to the surface of the structure. Water bleeding can cause water pockets below larger aggregate particles and under reinforcement. When the water content in the pore structure has decreased due to hydration and drying of the structure, these water pockets leave air-filled cavities under aggregates and reinforcement. Permeability of concrete is increased. Similarly, the density of concrete increases towards the bottom of the structure and shrinkage cracks are generated at the weak upper surface of the structure. This plastic settlement of the concrete ingredients can cause large cracks over the reinforcement bars at the upper surface, because reinforcement does not settle with the concrete consolidation.

When the bleeding surface water has evaporated, if very fine supplementary cementitious binders such as condensed silica fume have been used, the tensional forces generated on the surface pore water can cause severe plastic cracking at the upper surface. The capillary tension in pore water can be calculated by Kelvin's equation Equation [1.1] by using the relative water vapor pressure of the ambient environment. Pore water tension compresses concrete at the surface layer in the beginning. If the evaporation rate exceeds the bleeding rate, cracks form intruding deep into concrete and generating severe plastic cracks. This can be avoided by using a stiff enough concrete consistency and by using proper curing measures so that these cracks do not impair the durability properties of the concrete surface.

Shrinkage

During hydration of the binders and subsequent drying of concrete, large volumetric changes occur in different phases of the hardening concrete. These time-dependent shrinkage deformations cannot take place freely, and they are restrained by aggregate particles, reinforcement, or structural constraints. Tensional stresses are generated into the structure, and they can exceed the tensional capacity of the binder paste, initiating shrinkage cracks. If the crack widths are large, the penetration rate of water and deleterious substances into concrete is increased.

The cementitious reactions during hydration cause chemical shrinkage in the binder paste. Chemical shrinkage of cement is about 25% of the volume of chemically bound water, which is about 7% of the volume of the constituents participating in hydration reactions. This represents a linear deformation of about 0.1% in normal-strength concrete.

The free water consumption during hydration and the volumetric decrease in the binder paste due to chemical shrinkage cause self-desiccation in the pore structure of concrete. The curved water menisci in the capillary pores generate tension in the pore water, which causes a compressive stress state in the binder matrix and aggregates. Pore water tension can be calculated by Kelvin's equation Equation [1.1], if the relative pore water vapor pressure

is measured inside concrete. This autogeneous deformation caused by pore water tension is quite large for high-strength concrete in which the water/binder ratio is below 0.35. In these concretes, the relative water vapor pressure p_v/p_{v0} can be below 0.8. In high-strength concretes, autogeneous shrinkage cracks decrease the otherwise excellent durability properties. If the water/cement ratio is very low (0.17), autogeneous shrinkage can have a value of 0.7 %.

Evaporation of water from the surface of the concrete structure eventually dries the pore system. The volume changes are called drying shrinkage, and this is the dominating shrinkage mechanism in normal-strength concretes. The highly porous colloidal cement paste has very high surface area, and evaporation of pore water generates large shrinkage deformations. The final value of drying shrinkage can usually range from 0.3–0.6% in normal-strength concretes. During drying, the pore water tension differences between surface and interior concrete cause compression in the surface layer and tension inside the concrete.

The small amount of carbon dioxide in air reacts with calcium hydroxide in the pore water and eventually also other constituents of binder paste possessing CaO. This phenomenon is discussed in more detail in Section 1.4.1. Carbonation changes the pore structure of concrete and also generates carbonation shrinkage. Carbonation shrinkage can be as much as 30–50% of the total shrinkage of the surface layer of concrete. Part of the carbonation shrinkage is caused by the dissolution of $Ca(OH)_2$ crystals so that the compression caused in them by drying shrinkage is relieved. The forming calcium carbonate does not achieve any more similar compression.

Shrinkage takes place in the binder paste and, as aggregates do not shrink in a similar manner, differential shrinkage tensions generate cracks mainly in the interfacial transition zone (ITZ) between larger aggregates and bulk binder paste. The ITZ is more porous and weaker compared to bulk binder paste or aggregates and, therefore, cracks are generated into this zone. The ITZ is about 15–50 μm thick in normal-strength concretes.

Temperature gradients

During the hydration of massive concrete structures (dimensions over 0.7–1 m), hydration heat increases the temperature in the middle part of the structure when the concrete is 0.5–2 days old. At the same time, the strength and Young's modulus of concrete are increasing. If the ambient temperature of the environment is low, there can exist over 25 °C temperature differences at different parts of the structure. This generates compression at the middle part of the structure and tension at the surface which can cause cracking on the surface. Usually the crack widths are small (0.01–0.1 mm) and the crack depth into the surface layer of concrete is less than 50 mm.

However, the durability properties of the surface layers can be significantly compromised.

This crack formation can be hindered by selecting low-heat cements or by replacing a large portion of the cement by GGBS. Granulated blast furnace slag possesses much smaller hydration heat evolution. Also, replacing part of the cement by secondary cementitious binders such as fly ash can alleviate the tensional stresses at the surface. In very massive structures, heat insulation of the outer surface or even cooling of the inside of concrete by water pipe systems can be necessary.

During the cooling phase of the structure, concrete is shrinking, and this cooling shrinkage can be 0.2–0.4%. Comparing this with the other shrinkage deformations, it is of the same magnitude and can be an additional feature in shrinkage crack formation.

Heat treatment is a common way to increase the strength development rate especially in precast unit production. If the temperature rise or decrease rate in the process is large, this generates cracks into the structure. The coefficients of temperature expansion in water vapor, water, and binders and aggregates differ from each other by one and two orders of magnitude. The expansion differences in the different concrete phases are the reason for crack formation.

In older concrete structures, the temperature variations of the environment seldom cause cracking, if the structure is free to expand and the edge constraints do not hinder the deformations. However, in the design of certain bridge structures, for example, long-span box girders, temperature deformations have to be taken into consideration.

1.3.3 Mechanical abrasion, erosion, and cavitation

A common feature in this group of durability properties is that the deterioration mechanism is quite complicated and no simple tests that address all aspects of the phenomena are available. Mechanical abrasion of concrete surfaces can be caused in very different manners. The reason can be sliding of different materials on the surface, rolling of steel wheels, scraping motion of a machine, or percussion generated, for example, by studded tires of vehicles. In dams, off-shore structures, or industrial processes the action of abrasive materials carried by water, some other liquid, or ice leads to erosion of the concrete surface. Cavitation deterioration is caused by flowing water when the pressure in water changes abruptly. This damage mechanism has obtained its name because air cavities or bubbles collapse in flowing water generating a repeating, spike-like hitting pulse on the concrete surface.

Good-quality concrete surfaces that resist the durability loads belonging to this deterioration mechanism group have some common properties. Concrete compressive strength should exceed 35–40 MPa, and an increase

in compressive strength usually improves the wear resistance. However, the cement content should not exceed 350 kg/m^3 because normal good-quality aggregates have much better abrasion and erosion resistance compared with binder paste. The concrete mix should be proportioned so that risk of segregation is as small as possible. Extended curing always has a beneficial effect on the durability properties of these concrete structures. High-strength concretes or high-performance concretes are especially suitable concrete types for this group of structures.

In abrasion and erosion resistant concretes, the properties of aggregates are of vital importance. Strong and hard aggregates are preferred, and the gap-graded sieve curve used in proportioning the aggregates causes a situation in the surface layer of concrete in which a greater amount of large aggregates is at the surface. As aggregates have better abrasion resistance compared with cement paste, this improves the abrasion and erosion resistance of the concrete surface. Steel fibers and polymer concretes can be advantageous in structures prone to cavitation.

1.4 Chemically induced deterioration

Carbonation, corrosion of steel reinforcement, effects of acids and sulfates, delayed ettringite formation, and alkali–aggregate reactions are the chemical reactions causing deterioration of concrete structures which will be discussed in this section. Carbonation of the surface layer of concrete does not damage concrete as such. It is important because it reduces the pH value in the pore water. This is a prerequisite for corrosion of steel reinforcement in situations when there are no chlorides in concrete pore water. Similarly, the ingress of chlorides into concrete can be caused by physical means, but chlorides substantially enhance the corrosion of steel reinforcement and, therefore, their effects will be considered together with reinforcement corrosion.

1.4.1 Carbonation

Air contains a small amount of carbon dioxide (0.03% in rural areas and 0.3% in large cities) and it dissolves into the pore water of concrete producing carbonic acid. Carbonic acid reacts readily with calcium hydroxide situated in pore water in dissolved and crystalline form. Reaction products are water and $CaCO_3$ or its polymorphs aragonite and vaterite. Calcium hydroxide is mainly responsible for the high alkalinity of pore water in concrete (pH-value 12.4–13.5) while $CaCO_3$ is nearly neutral (pH ~ 7). In this way, carbonation decreases alkalinity in pore water. Carbonation reaction needs a suitable amount of water to proceed. The highest rate of carbonation occurs at a relative humidity between 50 and 70% in the ambient air. When concrete is very dry or nearly saturated, carbonation rate is minimal.

The reaction product of carbonation, $CaCO_3$, is larger than $Ca(OH)_2$ and, thus, the pore volume in concrete decreases when calcium carbonate precipitates on the pore walls of concrete. This decreases permeability of concrete. However, cracking caused by carbonation shrinkage mentioned in Section 1.3.2 impairs the decreased permeability, and it can be assumed to remain nearly unchanged with respect to carbonation.

When most of the available $Ca(OH)_2$ in the pore water has been consumed, C–S–H gel will also begin to disintegrate. Eventually, all concrete constituents possessing CaO in their structure will carbonate after a long time. The compressive strength of carbonated, normal-strength concrete remains nearly unchanged because $CaCO_3$ and its polymorphs also carry loads in a manner similar to that of the virgin concrete.

Carbonation of reinforced concrete structures poses no durability problems if the structure is situated in a dry environment, for example, indoors. However, if concrete is wet, carbonation of the reinforcement cover concrete can shorten the expected service lifespan significantly.

Alkalinity of pore water forms a thin passivity layer of oxide on the reinforcement steel surface. This passivity layer completely protects the reaction of steel with oxygen and water, and reinforcement bars in non-carbonated concrete do not rust. When carbonation has decreased the alkalinity of pore water near the surface of the steel bars to a pH value of approximately 9, the protective passivity layer on the steel surface is broken and, if oxygen and water are present, rusting of steel reinforcement begins (Fig. 1.6).

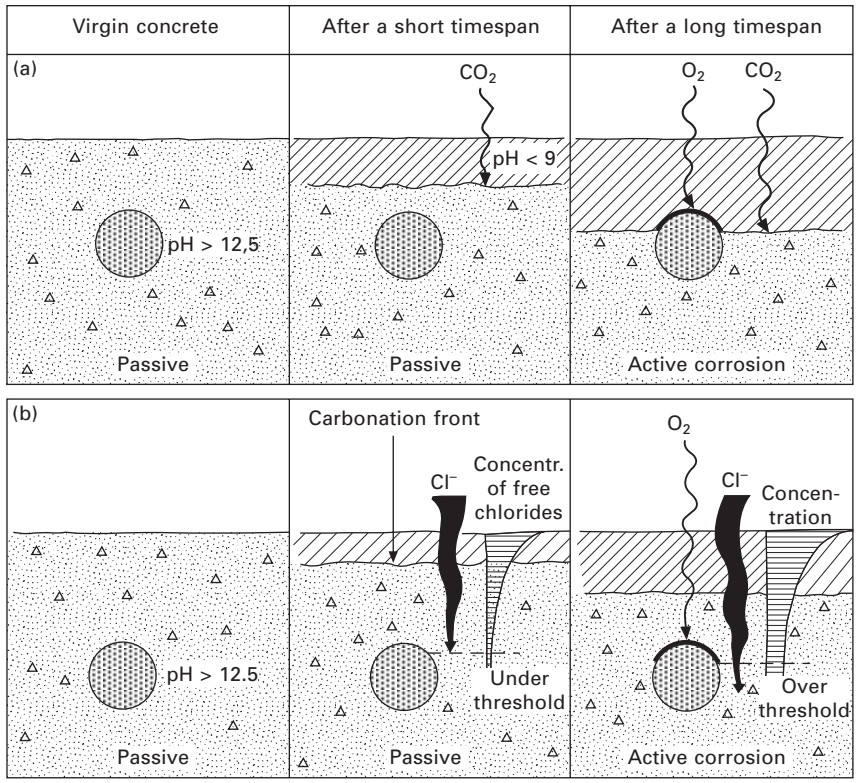
According to test results, the depth of the carbonation layer from the surface of the concrete structure increases in proportion to the square root of time if the environment of the structure is under steady hygrometric conditions:

$$x = k \cdot \sqrt{t} \qquad [1.4]$$

where x is the carbonation depth [mm], k is the carbonation coefficient [mm/year$^{0.5}$], and t is the exposure time [years]. This equation becomes effective after a couple of years carbonation.

The carbonation coefficient depends on the permeability of the surface layer of concrete and the relative humidity of the environment. When concrete is produced by using a low water/cement ratio, the carbonation rate decreases compared with low-strength concretes. If the surface is exposed to occasional rain so that the pore structure of concrete is nearly saturated part of the time, the carbonation rate is decreased compared with steady hygrometric conditions.

The form of the carbonation depth equation is such that the rate of the penetration depth of the carbonated layer decreases with increasing time. An increase in the thickness of the reinforcement cover layer effectively increases the estimated service lifespan of the reinforced concrete structure by increasing the reinforcement corrosion initiation time.



1.6 Corrosion initiation of concrete reinforcement caused by carbonation or chlorides when concrete is wet: (a) carbonation-initiated corrosion and (b) chloride-initiated corrosion (Fagerlund, 1987).

Four features which affect the carbonation rate have been examined above: carbon dioxide volume in the ambient air, permeability of the cover concrete over reinforcement, pore filling degree (moisture content) of the cover concrete, and the thickness of the cover concrete. The amount of CaO in concrete which can carbonate is obviously an important variable. The higher this CaO content is, the slower the carbonation rate. There is a big difference in CaO content which can carbonate in concretes produced by different blended cements. If the secondary cementitious binders are pozzolans such as fly ash or silica fume, they react with $Ca(OH)_2$ and form C–S–H, and the calcium hydroxide content in the concrete decreases. Therefore, concretes produced by blended cements are prone to carbonate faster than concretes produced by Portland cements. Similarly, if the binder contains a large amount of GGBS, there is a much smaller amount of CaO available for carbonation, and the carbonation rate is higher.

However, the permeability of these concretes produced by blended cements can be substantially reduced by increasing the hydration degree of the surface layer with prolonged and adequate wet curing. If the amount of these secondary cementitious binders is relatively small (fly ash < 30% or GGBS < 50% of the total binder amount) and adequate curing is applied, carbonation rate does not differ much from those concretes produced by pure Portland cements.

Sulfate-resisting cement leads to about 50% greater depth of carbonation compared to the situation when other Portland cements are used. Therefore, increased cover to reinforcement may be required.

1.4.2 Corrosion of steel reinforcement

Corrosion of steel reinforcement inside concrete can be initiated by two different mechanisms (Fig. 1.6). If there are no chlorides in the pore water, corrosion can be initiated when the carbonation front in the concrete cover over reinforcement has reached the steel bars. When the alkalinity in the pore water near reinforcement has decreased to the value of pH 9, the protective passivity oxide layer of $\gamma\ Fe_2O_3$ on the surface of the steel bars is broken and corrosion begins if water and oxygen are available on the surface of the reinforcement. Rusting of the reinforcement is a chemical reaction and, therefore, also a temperature-related phenomenon. In low sub-zero temperatures, the corrosion rate is considerably slower compared with the situation when the temperature is high (+20–40 °C).

The passivity protective oxide layer can also be broken, if the chloride content in pore water in the vicinity of the steel bars exceeds a certain threshold value which is dependent on the OH^--ion concentration of the pore water. Also, in chloride-initiated corrosion, water and oxygen must be available near the reinforcement surface.

After the initiation period, corrosion is an electrochemical process in which electrons and OH^--ions are transported between anode and cathode parts of the reinforcement and an electric circuit is formed. At the anode, positive metal ions Fe^{2+} are dissolved into the pore water and electrons move to the cathode via reinforcement. At the cathode, a chemical reaction takes place between electrons, oxygen, and water to form hydroxyl ions which move to the anode through pore water. At the anode, hydroxyl ions react with iron ions and $Fe(OH)_2$ or rust forms. There has to exist a difference in electrical potential between the anode and cathode as a driving force to sustain the reaction. Corrosion takes place only at the anode and, if the reaction can proceed freely, ferric hydroxide $Fe(OH)_3$ will form as the end product. The volume of the corrosion products can increase by a factor of over five which causes tensile stresses around the reinforcement bar. Eventually, in low-strength concretes, this can cause

cracking, spalling, or even delamination of the concrete cover over the reinforcement.

Cracks in the concrete cover have only a small influence on the service lifespan of the structure if there are no chlorides present and if the cracks are generated in a direction perpendicular to the reinforcement bars. This holds even if the crack width is relatively large. Corrosion products and re-alkalization in the crack over the reinforcement effectively hinder the advancement of corrosion. Concrete produced by a low water/cement ratio is, of course, more advantageous in this respect compared with concretes in which the water/cement ratio is high. If occasional mechanical loads are so severe that there is change in the crack width or if flowing water rinses the cracked surface, cracks will decrease the service lifespan of the structure.

When there is a chloride concentration exceeding a threshold value in the pore water, chloride ions break the protective oxide layer over the steel to form an anode, while the unbroken surface forms the cathode. During the chemical reaction, ferrous chloride is formed at the intermediate stage of the reaction, but, as ferrous hydroxide contains no chloride, Cl^- is regenerated by formation of HCl. In reality, the process of chloride-induced reinforcement corrosion is more complicated because drying of concrete and changes in moisture content affect the corrosion rate in a complicated manner (Raupach, 1996, 2006).

Only free chlorides in the pore water are effective in initiating the chloride-induced reinforcement corrosion. A part of the chlorides has reacted with the aluminates in the binder paste and is bound into the binder matrix. Hausmann (1967) has derived the relation between chloride content and OH^--concentration by studying reinforcement corrosion of steel in chloride/water solutions. Corrosion is initiated only if the concentration relation between chloride ions and hydroxyl ions is fulfilled, Equation [1.5]:

$$\frac{C_{Cl^-}\,(\text{mol/l})}{C_{OH^-}\,(\text{equiv./l})} \geq 0.6 \qquad [1.5]$$

OH^--concentration can be calculated by a formula derived by Tuutti (1982):

$$C_{OH^-} = \frac{c}{p} \cdot \left(\frac{\text{Na}}{23} + \frac{\text{K}}{39}\right) \cdot 100 \qquad [1.6]$$

in which c is cement content in [kg/m^3 concrete] and Na and K are wt% of soluble sodium and potassium, respectively, in the binder. Pore volume percentage in concrete is represented by p. Not only does this threshold value initiate reinforcement corrosion, but the moisture content in the concrete must be sufficiently high. Moreover, the permeability of concrete cover with respect to oxygen penetration has an effect on the beginning of the corrosion.

In chloride-induced reinforcement corrosion, cracking of the concrete cover layer substantially decreases the service lifespan of the concrete structure because then re-alkalization in the crack does not take place.

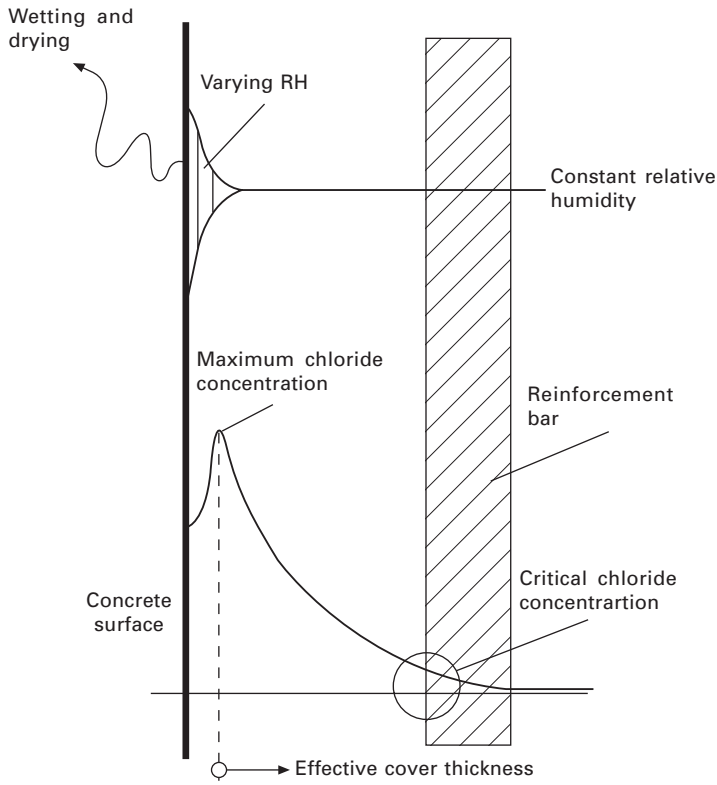
Penetration of chlorides into concrete

Reinforcement corrosion is one of the major deterioration mechanisms of reinforced concrete structures worldwide. The presence of chlorides increases the severity of the corrosion attack considerably. Chlorides can penetrate into concrete which is in contact with de-icing salts or seawater. Typical structures that are damaged by chloride-initiated reinforcement corrosion include bridges, car parking structures, and off-shore structures such as piers, dams, docks, and harbor structures.

Critical amounts of chlorides may also be present in the fresh concrete mix even though at present very few admixtures used in concrete contain chlorides. If seawater is used in producing concrete, chlorides are introduced into the mix.

When chlorides penetrate into concrete from outside, they are usually in a water solution. In moist concrete, the main transport mechanism is diffusion, but the capillary transport mechanism is also possible if concrete is exposed to drying and wetting cycles. Cyclic freeze–thaw loads can effectively increase the chloride content in concrete pore water. It is common practice to measure the maximum concentration of the chloride front penetrating from the surface of the concrete cover over reinforcement some centimeters inside the exposed surface (Fig. 1.7). Even though drying of concrete complicates the theoretical modeling of the phenomenon, Fick's second law is commonly applied in mathematical modeling of chloride intrusion into concrete.

The three most important variables that govern the chloride intrusion into concrete and the corrosion of the reinforcement are concentration of chlorides at the surface, concentration threshold value which initiates corrosion of steel, and the transport rate of chloride ions in the concrete cover layer. Without coating the surface of concrete, there are usually very limited means to decrease the concentration at the surface. If this chloride concentration is high, it is nearly impossible to hinder the penetration of chlorides to the reinforcement during long exposure times (50–100 years). At normal chloride exposure concentrations (seawater or de-icing agents), by selecting binders that cause a high OH^--concentration into pore water, the chloride threshold value that initiates corrosion of steel can be increased. Similarly, some binders react with chlorides and this decreases the free chloride concentration in pore water solution. These binders contain large amounts of C_3A or GGBS. This is only a temporary relief, because during carbonation large volumes of these bound chlorides dissolve back into pore water.



1.7 Chloride distributions in the surface layer of concrete (adapted from Sandberg, 1993).

The transport rate of chloride ions can be decreased by producing a more impermeable concrete cover by using lower water/cement ratio and by applying longer wet curing. The rate of chloride-induced corrosion is reduced considerably in structures situated in environments where relative humidity is less than 80%.

After initiation of chloride-induced reinforcement corrosion, it usually takes less than 10 years for the concrete cover surface to deteriorate to such an extent that repair measures have to be applied.

1.4.3 Reactions in binder paste and aggregates

The chemically induced deterioration mechanisms to be examined in this section are sulfate attack, acid attack, and alkali–aggregate deterioration reactions.

Sulfate attack

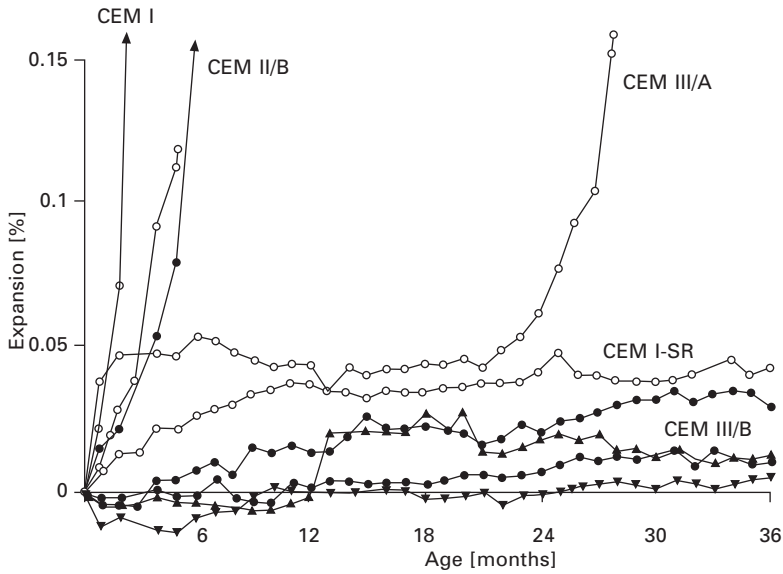
Sulfate attack is initiated when water-soluble sulfates (SO_4^{2-}), originating from ground or from seawater, penetrate into concrete pore water and react with aluminates or calcium hydroxide in cement paste. Reaction products expand remarkably which causes crack propagation and decreases the strength properties of concrete.

Four reaction mechanisms are responsible for sulfate damage in concrete. Sulfate ions can react with calcium hydroxide forming gypsum ($CaSO_4 \cdot H_2O$). Aluminates from cement or sometimes from aggregates can react with sulfates forming trisulfate (ettringite $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$). The increase in volume of the solid phases in these reactions is 124 and 227%, respectively.

The third sulfate deterioration mechanism is attributed to sulfate absorption into silicates or to a reaction with C–S–H. In these instances thaumasite ($CaSiO_3 \cdot CaCO_3 \cdot CaSO_4 \cdot 15H_2O$) is produced. This reaction takes place at low temperatures (Schneider *et al.*, 2003; Mielich and Öttl, 2004). The fourth mechanism does not need an outside source of sulfates to cause expansion and cracking into concrete. The deterioration mechanism can be termed inner sulfate attack caused by excessive heat treatment in concretes produced by Portland cement. When the temperature rises to 70–100 °C during hydration, ettringite transforms into monosulfate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) and sulfate. At lower temperatures, monosulfate becomes metastable and, if there is sufficient water available in hardened concrete or if the water content in the concrete subsequently increases, ettringite can again be formed. This reaction is accompanied by expansion in the concrete structure and subsequent cracking. This reaction can happen after a period of a couple years and, therefore, it is sometimes called delayed ettringite formation (Heinz, 1989; Stark *et al.*, 1992). This deterioration mechanism has been observed in façade precast units, concrete railway sleepers, and basement slabs.

The severity of sulfate corrosion expansion caused by outside sulfate attack is different depending on the salt composition. The severity increases in the order calcium sulfate, sodium sulfate, and magnesium sulfate. The severity of the attack increases also when the moisture content in concrete increases.

Sulfate attack can be mitigated by minimizing the C_3A content of the cement by applying sulfate resisting cements (Fig. 1.8). Sulfate resisting cements have a C_3A content below 3% or blast furnace slag content in the binder exceeds 70%. The other mitigation method is to reduce the $Ca(OH)_2$ content in concrete by applying blended cements in which the pozzolanic reaction decreases the calcium hydroxide amount.



1.8 Sulfate expansions of test mortars produced by different binders. The water : cement ratio of the mortars is 0.6, mortars have been immersed in sodium sulfate solution in which SO_4^{-2} content is 30 g/l (Frearson, 1986). The author has introduced contemporary cement-type notations into the figure.

Acid attack

Due to the high alkalinity of pore water (pH 12.5–14) in concrete, all binder paste constituents are stable in this environment. All strong acids (pH < 4.5) and many weak acids (5.5 < pH < 6.5) effectively decrease pore water alkalinity and attack $Ca(OH)_2$ and C–S–H gel of the binder paste. Most aggregates endure acid attack much better compared with the binder paste.

Acid attack is a surface phenomenon similar to carbonation and, therefore, the penetration depth is a function of the square root of time. The decomposition of hydration products forms new compounds which, if they are soluble, may be leached out from the structure. Some compounds can be disruptive as such, for example, H_2SO_4 is a combination of acid attack and sulfate attack.

In the case of weak acids, the severity of the attack cannot be evaluated by pH value only. Then one has to rely on a corrosion list of substances which attack concrete to varying degrees (Biczok, 1972; ACI 515.1R, 1985). No standard test procedures are available but, if comparative tests are performed, they should be carried out with the same concentration and composition of the acids that occur in the environment of the planned structure. Similarly, the flow rate of the solution and temperature should be comparable with the real planned structure. Accelerated tests are not recommended.

Pollution-induced acid rain consists mainly of nitric acid and sulfuric acid and is usually so dilute that it does not cause deterioration of concrete surface. However, if the pH value of acid rain is below 4.5, it can cause weathering of exposed concrete surfaces.

If sewage pipelines are not ventilated properly, bacterial growth can further a situation in which sulfuric acid is formed. The deteriorating portion of the concrete pipe structure occurs above the level of flow of the sewage.

Flowing pure water or ground water containing a small amount of CO_2 dissolves calcium hydroxide and causes surface erosion of concrete. Aggressivity of this water increases with the decreasing hardness (Ca^{2+}content/l) of the water (Gérard *et al.*, 2002).

Alkali–aggregate reactions

There are two reaction types causing deleterious swelling of concrete in moist environment due to reactions between alkalis (Na_2O and K_2O) and certain aggregates. In alkali–silica reaction, the reactive forms of silica are opal, chalcedony, and tridymite, which occur in opaline or chalcedonic cherts, siliceous limestones, and some volcanic rocks as rhyolites. Alkali–carbonate reaction is caused between some dolomitic limestone aggregates and the alkalis of the cement (Neville, 1995).

In both deleterious aggregate reactions, not all aspects of the mechanisms involved are known. Reactive siliceous minerals in the aggregate react with alkaline hydroxides originating usually from cement. Alkali–silicate gel is formed in the voids and cracks of the aggregate or on the surface of the aggregate. The gel absorbs water and swells in large volume (5–20%) if water is available in concrete and the environment. Internal pressures are generated into the concrete and eventually cracking can destroy the concrete structure totally. On the surface, cracks form a map-like pattern and sometimes pop-outs can be observed.

A combination of mix design features and moisture condition have to be fulfilled for the deleterious swelling of the gel to occur. The severity of the swelling of the gel depends on the amount of reactive material and on its particle size, alkali content in the pore water, and the moisture content in the concrete. For different reactive aggregates, particle size fraction, and cement type, a different pessimum combination can be found. If the reactive aggregate material amount in concrete is very small or very large and the moisture content is below a threshold value, the expansion caused by the swelling gel can be insignificant.

To hinder the alkali–silica reaction, the maximum relative humidity in the interior of concrete should not exceed 80–85%. The cement type should have as low a content of alkali oxide as possible. The equivalent Na_2O content in the cement should not exceed 0.60 (eqv. $Na_2O = Na_2O + 0.659 \cdot K_2O$ by

weight). Also, application of pozzolanic secondary cementitious binders has been shown to diminish the deleterious expansion caused by the alkali–silicate reaction.

The imperfectly understood damage mechanism in the alkali–carbonate aggregate reaction involves the de-dolomitization of the dolomite structure. When dolomite $CaMg(CO_3)_2$ structure is changed into $CaCO_3$ and $Mg(OH)_2$, it becomes more open and other minerals such as clay in the dolomite aggregate begin to expand due to moisture. Pozzolanic secondary binders are not effective in controlling the alkali–carbonate expansion which is contrary to alkali–silicate reaction. Fortunately, alkali–carbonate reaction is quite rare.

1.5 Summary

This chapter of the book deals with deterioration mechanisms in concrete and reinforced concrete. It can give the impression that a large number of concrete structures are subject to deterioration. However, most indoor concrete structures usually have no corrosion problems and their service lifespan can be measured in hundreds of years.

Outdoor concrete structures constitute about one-third of the total volume of concrete structures, and the major deterioration mechanisms that affect them are reinforcement corrosion and freeze–thaw deterioration. A large majority of the outdoor structures are not exposed to salts, and it is not difficult to design and build concrete structures that possess an estimated service lifespan of 200 years. The technology and design knowledge already exist to extend the estimated lifespan of outdoor structures exposed to chlorides to 100 years. All other deterioration mechanisms apply to concrete structures that comprise below 5% of the total concrete volume. Even in these structures, durability properties of concrete usually exceed those of the competing materials.

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