Corrosion in reinforced concrete structures

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Corrosion in reinforced concrete structures

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Preface

Reinforced concrete is a widely used construction material for bridges, buildings and platforms as well as for underground structures such as tunnels or reinforced concrete pipelines. In general, reinforced concrete is a very durable material capable of withstanding a large range of severe environments including marine, industrial and alpine conditions. Despite the fact that the majority of these structures show good long-term performance and high durability, there is still a large number of failures of concrete structures as a result of premature reinforcement corrosion. Owing to either carbonation of the concrete or the ingress of chlorides into the concrete, depassivation of the reinforcing steel occurs, leading to rapid steel corrosion with significant loss of cross-section. From a scientific point of view the depassivation of the reinforcing steel and the subsequent corrosion reactions are very complex due to various interactions of environmental exposure conditions, the different materials involved as well as the design of the structure. With regard to economical aspects the cost of corrosion damage to reinforced concrete bridges in the United States due to the use of deicing salts alone is estimated to be between \$325 and \$1000 million/year.[1] There are similar statistical results from Australia, Europe and the Middle East. In regions with a marine environment and warm climatic conditions the corrosion process may be significantly accelerated.[2]

The contributions in this book cover all the important aspects in the field of corrosion and corrosion protection of reinforced concrete and give new information on scientific and technological developments. The content is intentionally focused on the corrosion of reinforcing steel, therefore the

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[1] Transportation Research Board, (1991), Special Report 235, *Highway Deicing – comparing salt and calcium magnesium acetate*, Transportation Research Board, National Academy of Science, Washington, DC.

[2] Broomfield JP (2000), 'Corrosion of steel in concrete', in Winston R (ed.), *Uhlig's Corrosion Handbook*, 2nd ed., New York, John Wiley & Sons.

corrosion and deterioration of the concrete itself are not treated here. Furthermore, the durability of pre-stressed concrete is also excluded. The interested reader is referred to specialist publications covering this very specific topic.

This book discusses two major aspects of corrosion in concrete structures. In the first four chapters the basic processes and mechanisms of reinforcement corrosion including the important rate-controlling parameters are addressed, while in the following chapters new information on well-known and recently developed corrosion prevention techniques are provided. The primary aim of each contribution is to give an overview on the specific subjects. Each chapter provides readers with sufficient scientific and technological information so that they should be able to understand the subsequent practical applications also discussed in the chapter. In addition there are sections within chapters where interested readers will find additional detailed sources and references to literature on the specific topic. For readers with a wider interest in corrosion and corrosion protection the new edition of *Uhlig's Corrosion Handbook* is recommended.

In Chapter 1 the fundamental aspects of the corrosion process of steel in concrete, together with the most important factors influencing the corrosion process, are discussed. The overall corrosion process is highly complex; there are not only electrochemical and chemical reactions at the steel–concrete interface but there are also transport processes of aggressive substances and reaction products within the concrete. Until about the middle of the twentieth century carbonation of the concrete was the principal cause of reinforcement corrosion, leading mainly to more or less general corrosion of the reinforcing steel bars. At present, the chloride-induced corrosion due to extensive use of deicing salt or of severe marine environmental conditions is becoming increasingly important. In the case of chloride-induced corrosion the attack occurs very locally forming galvanic macrocells with usually high corrosion rates.

In Chapter 2 the various available nondestructive monitoring techniques are presented. In addition, newly developed online monitoring methods are also discussed. These methods are based on highly sophisticated computerised data acquisition and evaluation techniques. These allow, for the first time, direct measurement of the large influence of local environmental conditions on the corrosion propagation rates of real concrete structures. The results clearly show that the micro-climatic conditions on concrete structures determine to a large extent the corrosion behaviour of the reinforcement.

Corrosion studies on reinforced concrete structures are usually extremely time consuming and require very large specimens due to the heterogeneous structure of the concrete. Therefore numerical methods that simulate corrosion processes in reinforced concrete and allow parameter studies in addition to laborious experimental investigations have gained increasing attention in recent years. Chapter 3 gives an overview of the present state of the art on this topic. Besides empirical methods, models based on a sound electrochemical background are presented and the scientific as well as the practical significance are discussed.

The influence of composition and microstructure of concrete on the corrosion behaviour of reinforced concrete structures is discussed in Chapter 4. Besides Portland cement the use of modified cements as binder in concrete is increasing steadily. It is therefore important to know how these new binder types affect the transport of chlorides, the initiation of corrosion and the resulting corrosion rate. For this reason the results provided in this contribution are of fundamental importance in predicting the performance and durability of concrete structures using modified cements.

In the second part of this book different corrosion prevention methods are discussed, starting in Chapter 5 with the application of stainless steels as reinforcement materials. Various investigations and field tests have clearly shown that these alloys behave significantly better than does ordinary steel. When properly selected and handled on the construction site, excellent long-term performance can be expected. Stainless steel reinforcements have already been used in various countries. Application standards exist, for instance, in the UK, Germany, Denmark and Italy. Typical applications of stainless steel reinforcements are in those structures that are exposed to severe environments; for instance bridges in regions where deicing salts are used extensively. Chapter 5 also contains a section on fastening and connection elements where stainless steels are frequently used; within this application safety aspects are especially important.

Chapter 6 gives a comprehensive review of the fundamental aspects of corrosion protection methods by surface treatments and coatings. The contribution is structured according to a new European Standard EN 1504 currently in preparation. The authors discuss the different techniques now available as well as the necessary substrate preparation and quality assurance. This approach is doubtless very valuable for engineers and architects dealing with problems of durability at the design and construction stage and during repair work.

The last two chapters provide fundamental information on two specific topics that have gained increasing attention in recent years. In Chapter 7 the application of corrosion inhibitors is discussed in detail. The author provides the necessary scientific fundamentals and details of practical experience obtained with various corrosion inhibitors applied as admixtures into the concrete as well as on already existing structures. The discussion also includes environmental aspects that certainly have to be considered before this type of corrosion protection method is chosen.

With respect to repair work and maintenance of reinforced concrete structures, electrochemical techniques are of great interest. Chapter 8 gives an extensive overview on the mode and application of cathodic protection (CP), electrochemical chloride removal (ECR) and electrochemical realkalisation (ER). Advantages and limitations as well as economical aspects of these methods are discussed. Electrochemical techniques, only recently adopted for corrosion protection and maintenance of reinforced concrete structures, are certainly interesting and very promising tools; nevertheless, they must be evaluated very carefully before they are applied in practice.

In summary, this book contains not only all the important aspects in the field of corrosion and corrosion prevention of reinforced concrete but also discusses new topics and promising new developments. Furthermore, the contributions are based on a sound scientific background and the different topics have been critically discussed in view of practical applications. A combination of theory and practice makes this work a highly valuable tool for engineers and materials scientists.

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1

Corrosion in reinforced concrete: processes and mechanisms

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1.1 Introduction

The conditions which lead to corrosion of steel in reinforced concrete structures are becoming well understood. Nevertheless, many existing concrete structures show significant corrosion, often when comparatively new, leading to the need for expensive repair. In most cases either the structures were not durable enough or the appropriate maintenance had been neglected. Corrosion of the reinforcement embedded in concrete causes most of the failures of concrete structures. Up to the 1950s carbonation of concrete was the main cause of corrosion. Since then chloride-induced corrosion has become much more important for structures exposed to chloride-containing environments (deicing salt, a marine climate, salt-contaminated aggregates).

The following sections give fundamental information on the corrosion process of steel in concrete and the most important factors influencing the corrosion rate. Furthermore, the mechanisms of transport of chloride and water in concrete are described. Some general aspects of corrosion prevention and protection measures are included. The corrosion and the deterioration processes of concrete itself are not treated in this chapter.

1.2 Basics of corrosion of reinforcement in concrete

1.2.1 General aspects

The high alkalinity of the concrete pore water (pH over 12.5) leads to a passive layer forming on the steel that reduces the corrosion attack to negligible values. As long as this passive layer is sustained, corrosion will not occur. Two processes may destroy this protection layer:

- Carbonation of concrete.
- Chloride attack.

Corrosion of the reinforcement can show different forms, ranging from widespread general corrosion to a very local attack (pitting corrosion). General corrosion, mostly in cases of carbonated concrete, leads to early cracking and spalling of the concrete, often with comparatively little reduction of the cross-section of the reinforcing steel bars, whereas the localised corrosion due to chloride ions results in pits, randomly distributed along the steel bars (Fig. 1.1a and b). The depth of such pits may be large before signs of deterioration of the concrete surface can be seen.

1.2.2 Conditions for corrosion

There are four conditions that must be fulfilled to start and maintain the corrosion process. These are summarised in Table 1.1 and in Figs 1.2 and 1.3.

1.2.3 Corrosion as an electrochemical process

The corrosion of metals is an electrochemical process (Fig. 1.3). For steel in concrete the following reactions occur:

anodic reaction: $$2\mathrm{Fe} \rightarrow 2\mathrm{Fe}^{2+} + 4\mathrm{e}^- \qquad [1.1a]$$

cathodic reaction: $$\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^- \rightarrow 4\mathrm{OH}^- \qquad [1.1b]$$

sum of the reactions: $$2\mathrm{Fe} + 2\mathrm{H}_2\mathrm{O} + \mathrm{O}_2 \rightarrow 2\mathrm{Fe(OH)}_2 \qquad [1.1c]$$

The anodic reaction represents the dissolution of the metal. The flux of ions and electrons respectively can be taken as a measure of the corrosion rate. This can be given as mass lost per unit of time and area, as reduction of the thickness per unit of time or as current density (current per unit of area). For iron and steel the following statements are valid:

Iron/steel: $1\,\mathrm{mA/cm^2} \simeq 11.6\,\mathrm{mm/year} \simeq 250\,\mathrm{g/m^2\ day}$
$1\,\mu\mathrm{A/cm^2} \simeq 12\,\mu\mathrm{m/year} \simeq 0.25\,\mathrm{g/m^2\ day}$

1.2.4 Corrosion potential

The corrosion potential of a metal in a specific electrolyte has a characteristic value. From Table 1.2 containing some values for steel, stainless steel, copper and galvanised steel in concrete it can be seen that the corrosion potential of steel in concrete may differ over several hundreds of millivolts.

1.2.5 Corrosion initiation and propagation

The reinforcement in young concrete structures is fully protected: the pH of the pore water is high (Fig. 1.4) and there is only a small quantity of

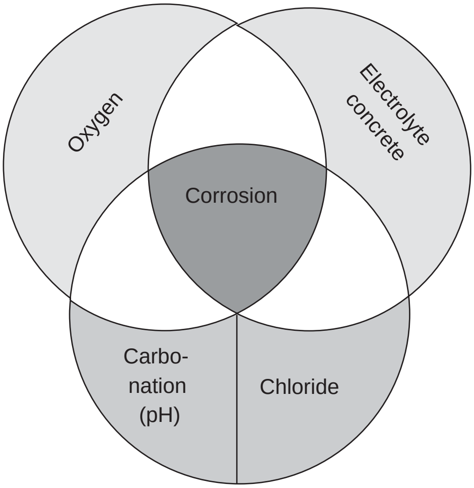
(a)

(b)

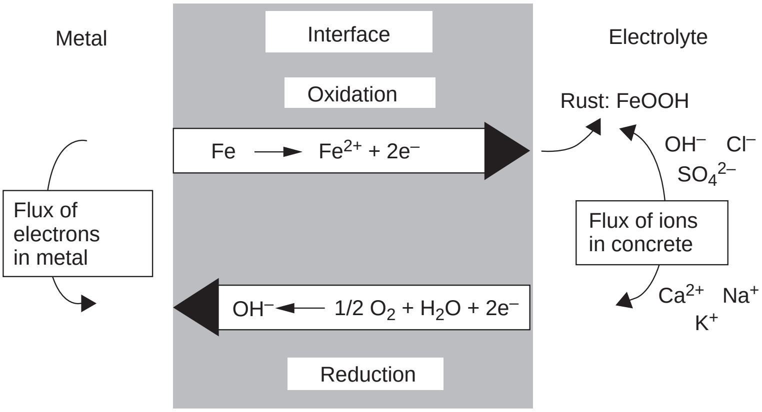
1.1 Corrosion of reinforced concrete girders of bridges. (a) Spalling of concrete due to carbonation and chloride ions; (b) Heavily corroded and one cracked prestressing steel wire due to chloride-induced corrosion.

Table 1.1 Conditions for corrosion of steel in concrete

	Condition for corrosion of steel in concrete	Condition is fulfilled, if:
1	An anodic reaction is possible.	The passive layer of the steel bar breaks down and depassivation of the steel occurs. This can be caused by carbonation of concrete (lowering the pH of the pore water) and ingress of chloride into the concrete, reaching a critical level.
2	A cathodic reaction is possible.	Oxygen as the driving force of the corrosion process is available at the interface of the reinforcement in a reasonable amount.
3	A flux of ions between the site of the anodic reaction and the site of the cathodic reaction is possible.	The environment or electrolyte between the site of the anodic reaction and the site of the cathodic reaction conducts well.
4	A flux of electrons is possible.	There is a metallic connection between the sites of anodic and cathodic reactions. For monolithic reinforced concrete structures this condition is usually fulfilled.



1.2 Conditions for corrosion of steel in concrete.



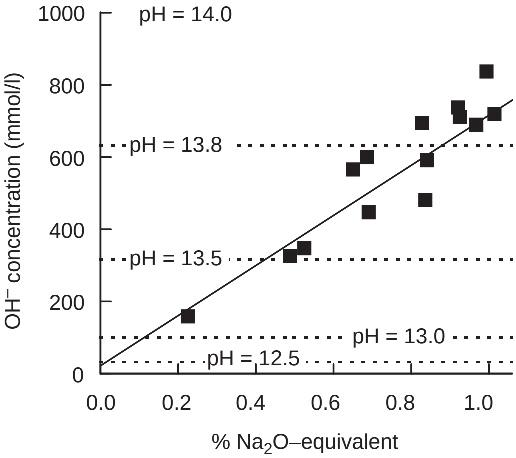
1.3 Corrosion as an electrochemical process (Hunkeler 1994).

Table 1.2 Corrosion potentials of metals in concrete (Hunkeler 1994)

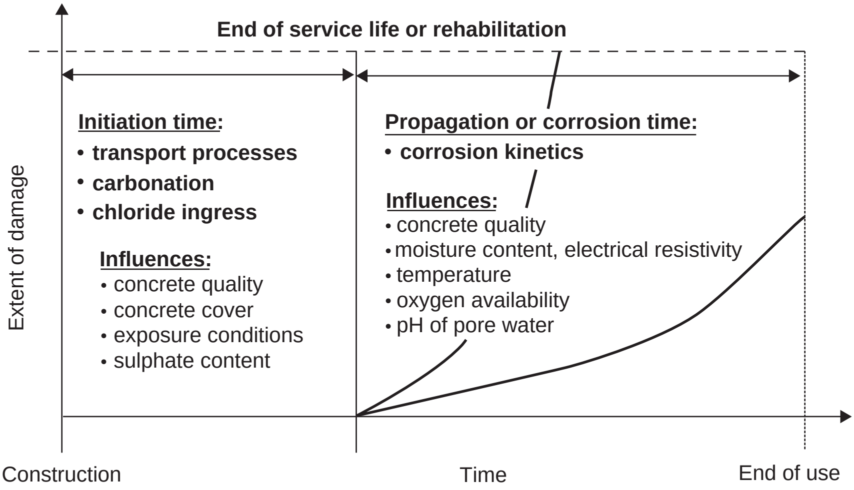
Electrode/Metal	Corrosion potential, mV_{CSE}		
Reinforcing steel bar in:			
saturated $Ca(OH)_2$ solution			–1.1
O_2-free, water-saturated concrete			≥–1.1
humid, Cl^--containing concrete			≥–0.6
humid, Cl^--free concrete	+0.1	to	–0.1
humid, carbonated concrete	+0.1	to	–0.3
dry, carbonated concrete	+0.2	to	0
dry concrete	+0.2	to	0
Stainless steel in humid concrete	+0.1	to	–0.2
Copper in humid concrete	+0.1	to	–0.2
Zinc coated steel in:			
wet concrete			≥–1.1
humid, Cl^--containing concrete			≥–0.8
humid concrete	similar to reinforcing steel		
humid, carbonated concrete	+0.2	to	–0.1
dry, carbonated concrete	similar to reinforcing steel		
dry concrete	similar to reinforcing steel		

chloride ions in the concrete if no chloride-contaminated components for the concrete production have been used (e.g. chloride-containing water, aggregates or admixtures). Some time must elapse before the conditions in the concrete are such that corrosion may start (Fig. 1.5).

For a given concrete quality the corrosion rate after the initiation (propagation or corrosion phase) depends mainly on the following factors (see Section 1.8):



1.4 OH–concentration of the pore water of cement pastes as a function of the Na_2O-Equivalent (Na_2O_{Eq} = %Na_2O + 0.659 K_2O) (Hunkeler 1994). Data from Page (1992).



1.5 Extent of corrosion damage over time. The initiation period depends on a variety of parameters such as concrete quality and concrete cover. The propagation period is governed mainly by the electrolyte resistance influenced by temperature and moisture content and to a smaller part by electrochemical reaction resistances.

- Moisture content and resistivity of concrete.
- Temperature.
- Oxygen availability.
- pH of pore water.

The chloride content itself has a minor influence on the corrosion process.

1.3 Availability of oxygen

1.3.1 Influence of the moisture content of concrete

Meanwhile, the content of oxygen in the air is more or less constant; it may vary in concrete locally and with time over orders of magnitude. The content and the diffusion coefficient of oxygen in concrete depend mainly on the concrete quality or permeability and on the moisture content of the concrete. Besides this the access of air to the concrete surface, the salt content and the temperature may have some influence as well. In concrete with a high moisture content the diffusion coefficient of oxygen $D(O_2)$ is very low since oxygen has to diffuse through the water in the pores which is a much slower process than in the empty, air-filled pores.

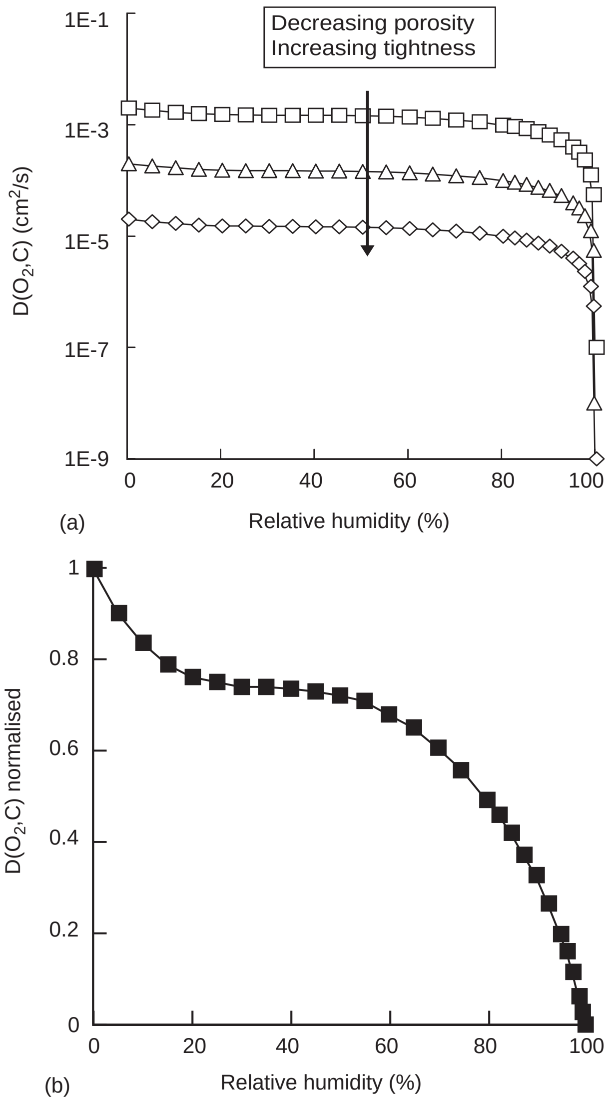
In water $D(O_2)$ is approximately four decades lower than in air ($\approx 10^{-5}\,cm^2/s$ in water compared to $\approx 0.2\,cm^2/s$ in air). Since there is lack of systematic investigations on the important influence of the moisture content on $D(O_2,C)$ an attempt has been made to calculate the diffusion coefficient of oxygen in concrete $D(O_2,C)$ as a function of the moisture content of the concrete (Hunkeler 1994). With the equation from Maxwell used for resistivity calculations the influence of the moisture content may be roughly estimated with Equation 1.2 (Hunkeler 1994).

$$D(O_2,C) = \frac{D_L\left(\frac{D_L}{D_W} - W\frac{D_L}{D_W} + 3\right)}{2W\left(\frac{D_L}{D_W} - 1\right) + \frac{D_L}{D_W} + 2} \qquad [1.2]$$

where:

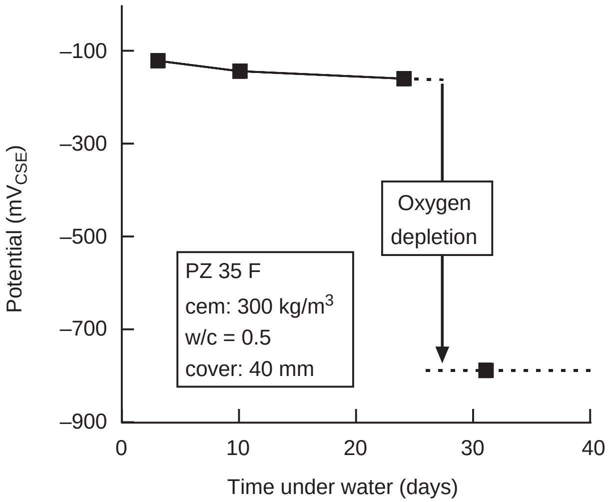
$D(O_2,C)$ = oxygen diffusion coefficient in concrete, cm^2/s
D_L = oxygen diffusion coefficient in dry concrete, cm^2/s
D_W = oxygen diffusion coefficient in wet concrete, cm^2/s
W = water content of the concrete, vol.%.

The results are shown in Fig. 1.6(a and b). The curves in Fig. 1.6a are primarily dependent on the porosity of the concrete (determines the vertical position, *y*-axis) and the adsorption isotherm (determines the shape, *x*-axis). For the calculation it was assumed that the effective $D(O_2)$ in concrete is



1.6 (a) Diffusion coefficient of oxygen $D(O_2,C)$ as a function of the relative humidity (Hunkeler 1994). The water content corresponding to a given RH was taken from the adsorption isotherm in Fig. 1.9; (b) Normalised diffusion coefficient $D(O_2,C)$ as a function of the relative humidity (Hunkeler 1994).

reduced by a factor of 10^2 to 10^4 compared to values in free air or water. The curves shown in Fig. 1.6 are basically in agreement with experimental results (Houst 1992, Houst and Wittmann 1994, Ehrenberg and Diederichs 1994, Kropp and Hilsdorf 1995). It has to be pointed out that for a given



1.7 Corrosion potential of steel in concrete as a function of time under water (Hunkeler 1994). Data from Raupach (1992).

concrete this type of calculation can only be carried out if the adsorption isotherm of a specific concrete is known.

1.3.2 Oxygen depletion

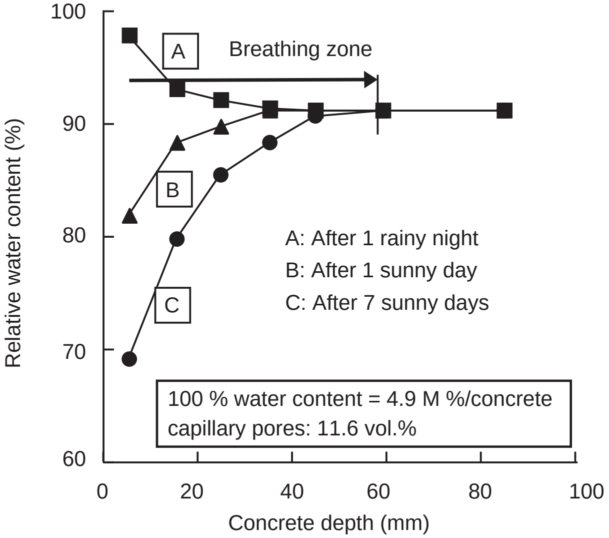
When concrete is thoroughly water saturated, i.e. when it has been in permanent contact with liquid water for a long time, the pores are filled with water, with the exception of the large air and compaction pores. This reduces the access of oxygen to the steel surface to very low values. With the depletion of oxygen the corrosion potential of steel in concrete falls from high to very negative values (Fig. 1.7).

1.4 Concrete as electrolyte

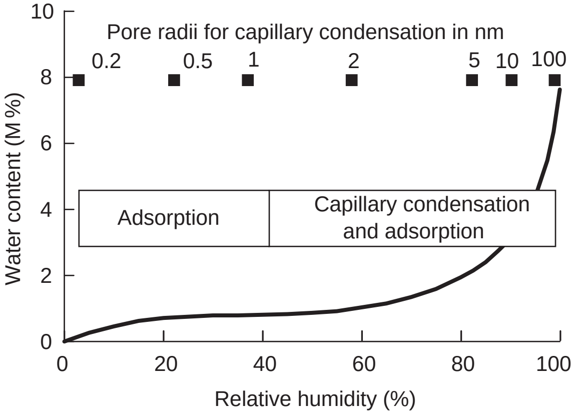
1.4.1 Moisture content – adsorption isotherm

Porous materials such as concrete may adsorb water from the air or desorb it to the air again. Figure 1.8 shows that concrete takes up water during a rainy day and loses it afterwards when it is warm and dry. For the adsorption and desorption processes the determining factors are the pore structure (pore radii and their distribution), the pore water composition and the relative humidity of the air (RH).

The pore structure of concrete and the pore water composition are influenced by a variety of parameters (Hunkeler 1994). The most important of these are:



1.8 Water content in cover concrete after a rainy night and after dry summer days (Hunkeler 1994). Data from Rehm (1988).



1.9 Typical sorption isotherm of concrete (Hunkeler 1994, and Hunkeler and Holtzhauer, 1994).

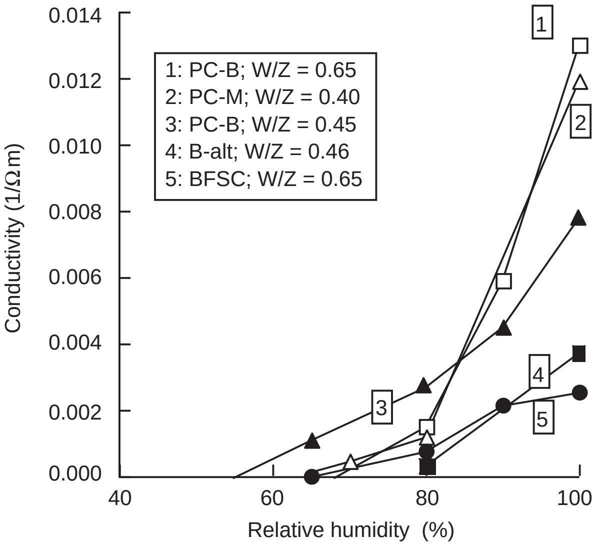
- Type and content of cement, chemical admixtures and mineral additions (e.g. fly ash, silica fume).
- Water to cement ratio.
- Curing conditions.
- Age.

In Fig. 1.9 a typical adsorption isotherm is shown. Up to RH of approximately 40 % the water uptake is basically an adsorption process at the inner surface of the concrete pores. A monolayer of water molecules is built up, which is strongly bonded to the surface by adsorption forces. These water molecules are less mobile than the water which concrete may take up at RH >40 % by capillary condensation caused by capillary forces.

1.4.2 Resistivity and conductivity of concrete

The moisture content of the concrete, together with the pore structure and pore water composition, determines the resistivity of the concrete ρ_C, which is important for the corrosion process (Hunkeler 1993, Hunkeler 1994, Hunkeler and Holtzhauer 1994). Figure 1.10 shows the conductivity σ_C (= reciprocal value of the resistivity ρ_C) as a function of RH of different types of cementitious materials. These σ_C-RH-curves reflect the different adsorption isotherms of the various materials. It is clearly visible in these figures that σ_C drastically decreases with decreasing RH and approaches zero at a relative humidity between 40 and 80 %.

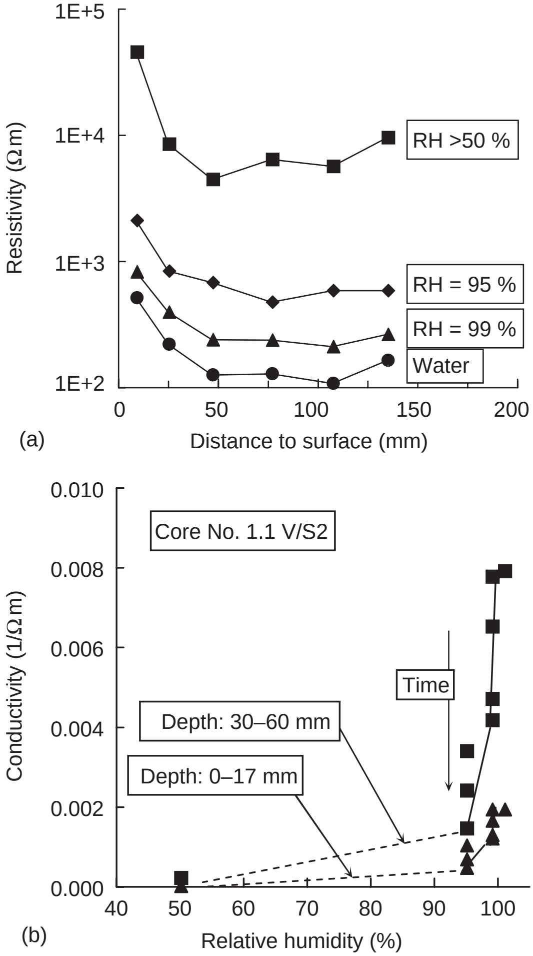
For the Portland cement concrete it may be concluded that the σ_C-RH-curves are steeper the higher the w/c-ratios are. Comparing the young and old concrete with the same w/c-ratio the curve for the old concrete (B-alt) is shifted towards lower σ_C-values. The shift is approximately parallel. There is no general correlation between the resistivity and the total pore volume



1.10 Dependence of the conductivity on the relative humidity of various mortars and concretes (Hunkeler 1993).

since not all the water in the pores is mobile and its composition depends on the concrete mix.

Figure 1.11a shows the resistivity profile of a core stored under different conditions (temperature: approximately 20 °C). A pronounced increase of the resistivity is noticed at the outer surface of the core. This increase is caused by the carbonation of the concrete in the cover zone. The σ_C-RH-curves in Fig. 1.11b represent the outer part of the concrete in a depth of 0 to 17 mm (concrete cover) and of about 30 to 60 mm. At RH = 99 % the last measurements were made after 2 months, at RH = 95 % after 4 months.

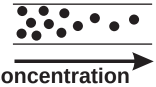
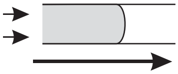


1.11 (a) Resistivity of a concrete core as function of the storage conditions (relative humidity RH) (Hunkeler 1997); (b) Conductivity as function of the relative humidity (Hunkeler 1997).

1.5 Transport processes in concrete

1.5.1 Transport mechanisms

The transport of gases (O_2, CO_2), water and ions (chloride, Cl^-) in concrete is only possible in cracks, gravel neats and the pore system. It is caused by capillary forces, gradients of pressure (gases, water) or of concentrations (ions), absolute pressure difference (water, gases) and migration (Fig. 1.12, Table 1.3). The characteristic parameters of these transport processes are

Transport processes in concrete		
Type	**Driving force**	**Pores**
Diffusion (gases and ions)	 **concentration gradient** dc **Partial pressure difference** dp	**Filled with air or water**
Capillary suction (liquids)	 **Surface tension** s **Contact angle** q	**Filled with air**
Permeation (gases and liquids)	 **Absolute pressure difference** dp	**Filled with air or water**

1.12 Transport processes in concrete, based on Paschmann et al. (1995).

Table 1.3 Transport processes in concrete and their characteristic parameters (Hunkeler 1994)

Transport mechanism	Driving force	Transport coefficient	Symbol [unit]
Capillary suction	Capillary forces	Water uptake coefficient Water penetration coefficient	W_A [g/m^{2}s$^{0.5}$] W_E [m/s$^{0.5}$]
Ion diffusion	Concentration gradient	Diffusion coefficient	D [cm^2/s]
Gas diffusion	Partial pressure difference		
Gas flux	Absolute pressure difference	Permeability coefficient	K_P [m^2]
Water flux		Darcy coefficient	K_D [m/s]
Migration	Electrical direct voltage field	Ion mobility (transport number of ion b)	u_i [cm^2/V s] (t_b)

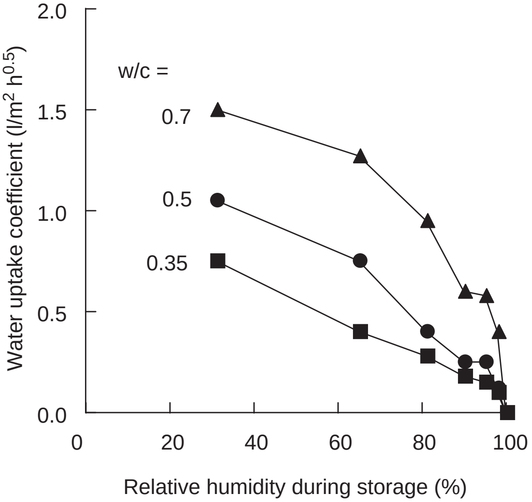
Table 1.4 Ion mobility of some cations and anions (Elsener 1990)

Cation	u_i [cm^2/V s]	Anion	u_i [cm^2/V s]
H^+	36.3 10^{-4}	OH^-	20.5 10^{-4}
K^+	7.6 10^{-4}	Cl^-	7.9 10^{-4}
Na^+	5.2 10^{-4}	HCO_3^-	4.6 10^{-4}
1/2 Ca^{2+}	6.0 10^{-4}	1/2 SO_4^{2-}	8.3 10^{-4}

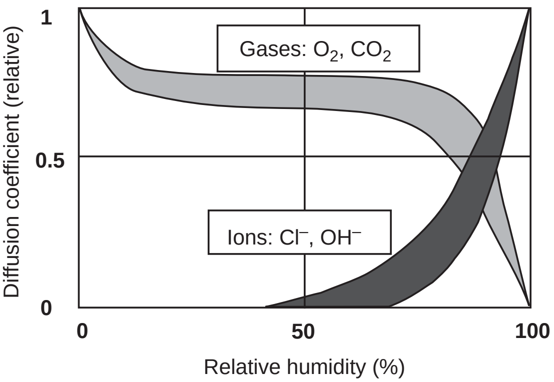
the water suction and penetration, diffusion and permeability coefficient and ion mobility (Table 1.4). Although the coefficients of the transport processes do not all depend in the same way on the pore structure there are some relations between the different coefficients.

1.5.2 Influence of the relative humidity

Capillary suction and diffusion processes are very important for the uptake of chloride and the carbonation reaction and thus for the corrosion process. Capillary suction is more efficient for dry than for wet or humid concrete (Fig. 1.13). The diffusion coefficient of ions increases with the moisture content of the concrete (the mobility of ions is greatest in completely water-filled pores), whereas it decreases for gases (Fig. 1.14).



1.13 Influence of the relative humidity during storage and the w/c ratio on the water uptake coefficient W_A of concrete. Data from Major (1993).



1.14 Influence of the relative humidity and moisture content of concrete, respectively, on the diffusion coefficients of gases and ions (schematic drawing). The increase and decrease, respectively, are primarily influenced by the sorption isotherm (Hunkeler 1994).

1.5.3 Transport processes under practical conditions

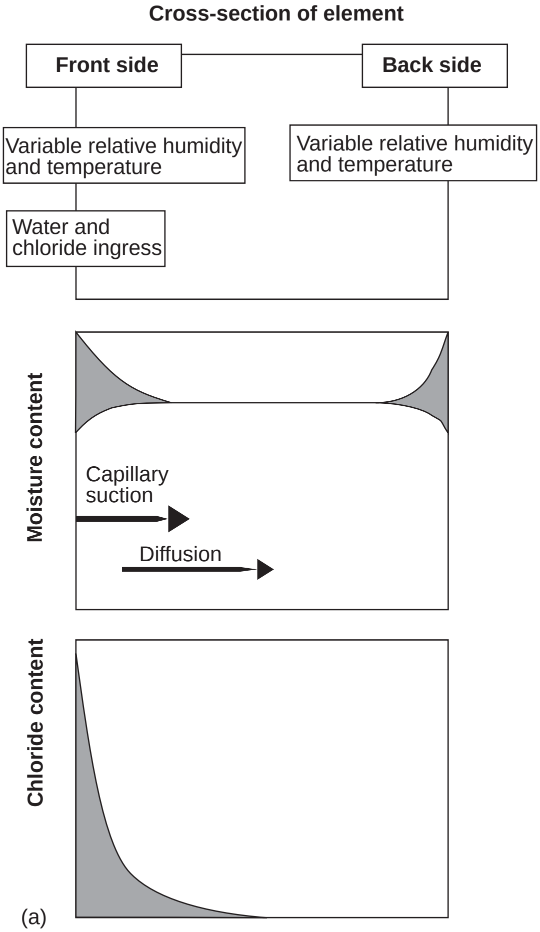
Figure 1.15 (a–d) on pages 16–19 shows different situations of the water and chloride transport in and across a concrete element. Under most practical conditions chlorides are transported in concrete by capillary suction and diffusion. In completely water-saturated concrete diffusion is the only transport process. The movement of water and ions (chloride) through a concrete element is mainly governed by differences between the moisture content of the front side (side exposed to rain, splash water etc.) and that of the unexposed back side. Capillary suction is the main mechanism for the uptake of water and chloride in the outermost concrete zone (cover concrete). Deeper in the concrete diffusion is the dominant transport mechanism. Dependent on the differences of the moisture content of the front and back side the transport of chloride in the inner zone of the element is favoured or hindered.

For reinforced concrete components in chloride-containing water, the water and chloride movement is upwards to the zone where the water can evaporate. In the evaporation zone the chlorides remain in the concrete. Therefore, the highest chloride levels are usually found just above the water level.

1.6 Corrosion induced by carbonation of concrete

1.6.1 Chemical reactions

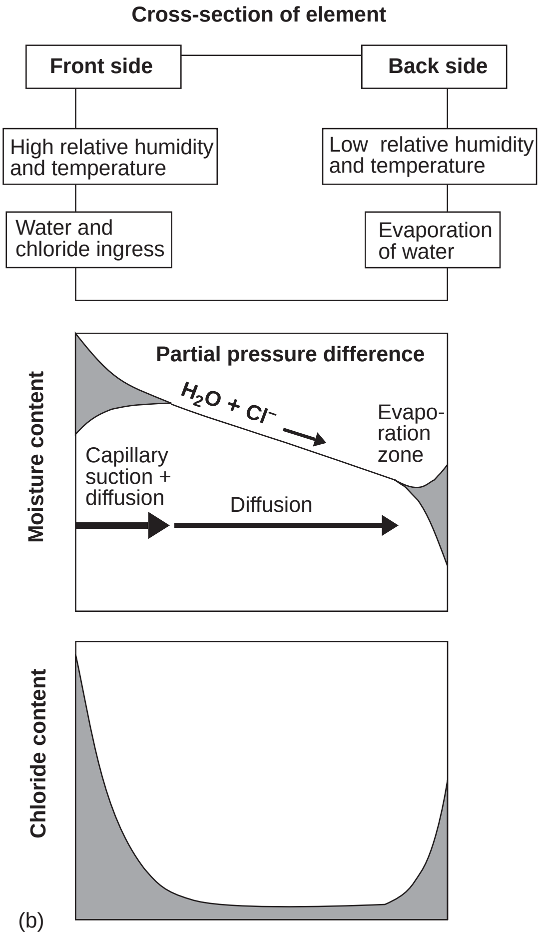
The carbonation of concrete is a consequence of chemical reactions of the alkaline components of the cement paste (e.g. NaOH, KOH, $Ca(OH)_2$ and



1.15 Chloride and water transport in and across a concrete element (Hunkeler 1994).

calcium-silicate hydrates) with the atmospheric carbon dioxide (CO_2). These reactions can only occur in the presence of a certain amount of water. Here the pH of the pore water decreases from the original value above >12.5 to values between 6 and 9 (Fig. 1.16). The pH stays at the value of the saturated $Ca(OH)_2$-solution, i.e. around 12.5, as long as not all $Ca(OH)_2$ has reacted. Therefore, the content of $Ca(OH)_2$ of concrete is a decisive parameter of the carbonation resistance of concrete since it determines the time of the decrease of the pH to values below 12.5.

During the carbonation the following reactions may occur (Hunkeler 1994):



1.15 Continued

Uptake of CO_2 in the pore water (formation of carbonic acid)

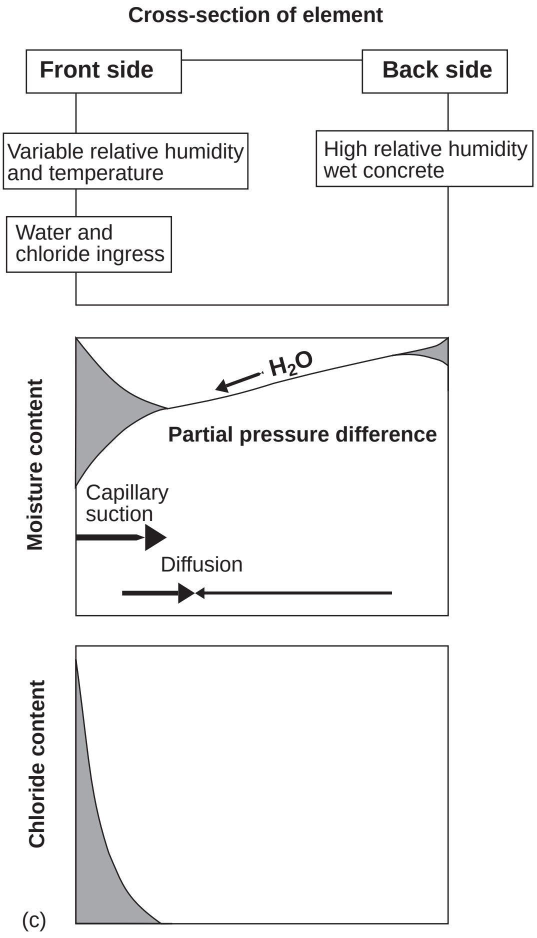
$$CO_2 + H_2O \rightarrow 2H^+ + CO_3^{2-} \tag{1.3}$$

Dissolution of alkaline constituents of the pore water

$$NaOH \rightarrow Na^+ + OH^- \tag{1.4a}$$

$$KOH \rightarrow K^+ + OH^- \tag{1.4b}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^- \tag{1.4c}$$



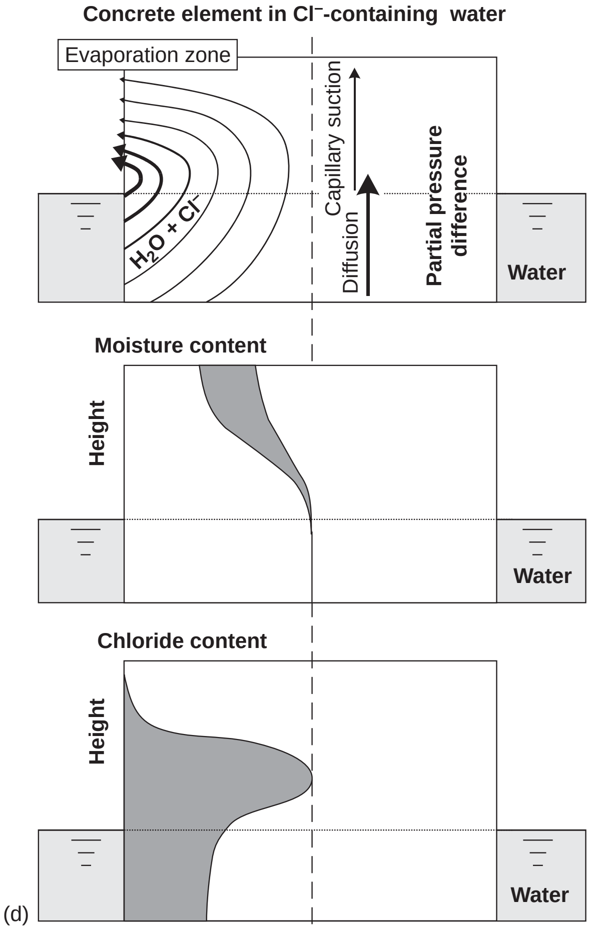
1.15 Continued

Full reaction (reaction releases water)

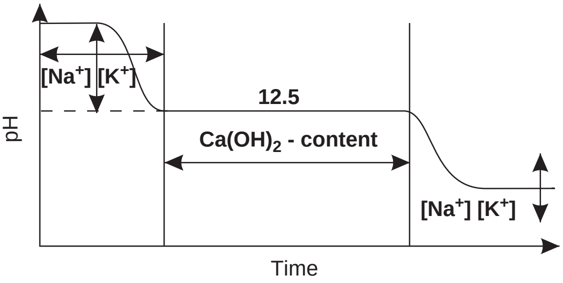
$$2NaOH + H_2O + CO_2 \rightarrow Na_2CO_3 + 2H_2O \quad [1.5a]$$

$$2KOH + H_2O + CO_2 \rightarrow K_2CO_3 + 2H_2O \quad [1.5b]$$

$$Ca(OH)_2 + H_2O + CO_2 \rightarrow CaCO_3 + 2H_2O \quad [1.5c]$$



1.15 Continued



1.16 Changes of the pH of the pore water with time due to the carbonation of concrete (schematic); [Na^+], [K^+]: concentration of the Na^+ and K^+ ions.

Since the solubilities of Na_2CO_3 and of K_2CO_3 are much higher than that of $CaCO_3$ they remain dissolved in the pore water, whereas $CaCO_3$ is deposited. With the ongoing carbonation the carbonates react further, if there is enough CO_2 and water available, to soluble hydrogencarbonate (HCO_3^-, bicarbonate). This leads to a further reduction of the pH.

Carbonate–bicarbonate equilibrium (reaction takes in water)

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3 \qquad [1.6a]$$

$$K_2CO_3 + H_2O + CO_2 \rightarrow 2KHCO_3 \qquad [1.6b]$$

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2 \qquad [1.6c]$$

The simultaneous presence of CO_3^{2-} and HCO_3^- ions buffers a further decrease of the pH as long as carbonates are still available. The equilibrium of the reactions according to Equations 1.6a to 1.6c depends on the content of CO_2 in the air, on the temperature and on the moisture content of the concrete. In relatively dry rooms in buildings the pH of concrete is not reduced as much as it is in concrete out of doors exposed to rain. The pH of reaction according to Equation 1.6c is for a content of CO_2 in the air of 0.03 vol.% around 8.5, for content of CO_2 1 vol.% around 7 and in pure CO_2 atmosphere around 6. The pH values of the reaction according to Equations 1.6a and 1.6b are about one pH unit higher.

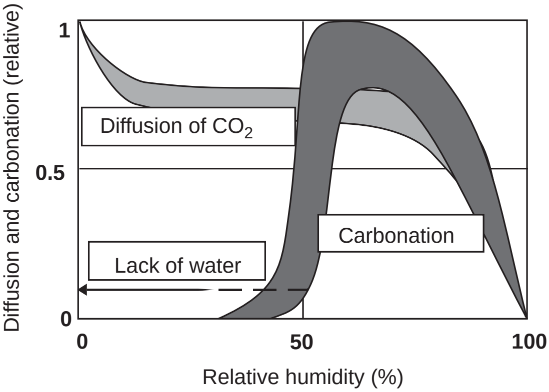
The final pH, which is reached after a complete carbonation, depends therefore mainly on the following parameters (Hunkeler 1994):

- Alkali content of the cement (Na_2O, K_2O).
- Degree of hydration of the cement.
- Moisture content of concrete.
- Partial pressure of CO_2.
- Temperature.

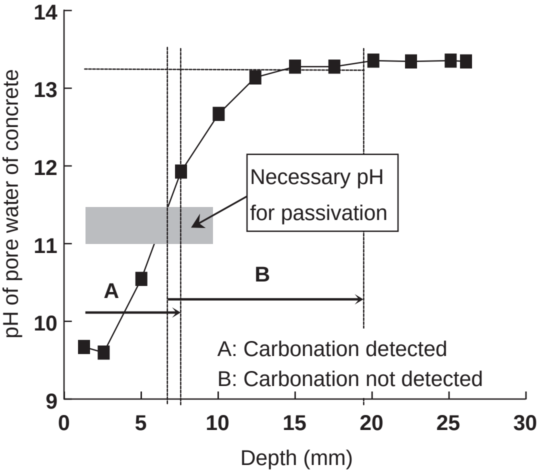
Besides CO_2 other gases such as sulphur dioxide (SO_2) or nitric oxides (NO_x) may contribute to the neutralisation reaction. The contribution of these gases is usually small because the content of SO_2 or NO_x in the air is generally much lower than that of CO_2.

1.6.2 Influence of moisture content

Since the diffusion of CO_2 is low at high moisture content of the concrete and the carbonation reaction needs water there is a maximum rate of carbonation at a medium range of relative humidity (Fig. 1.17).



1.17 Relative diffusion coefficient of CO_2 and relative rate of carbonation as a function of relative humidity (schematic) (Hunkeler 1994).



1.18 pH of pore water as a function of depth. Results of a pore water analysis (Page 1992). A: carbonation detected, B: carbonation not detected by the phenolphthalein test (pH indicator) (Hunkeler 1994).

1.6.3 Carbonation profile

The carbonation of concrete starts at the surface and can advance to greater depth until it reaches the reinforcement (Fig. 1.18). For a durable corrosion protection of the reinforcement a pH of 11 to 11.5 is necessary. If the pH drops to lower values the reinforcing steel bars may start to corrode. In practice phenolphthalein indicator is used to determine the carbonation front, but this does not detect the complete gradient. As shown in this figure the whole pH gradient is approximately 20 mm, but the pH indicator gives only a value between 6 and 7 mm.

1.6.4 Time laws for carbonation

There are many papers on the time dependency of the carbonation of concrete and by the 1960s a simple equation based on Fick's first law had been derived (Schröder et al. 1967, Schiessl 1976, Kropp and Hilsdorf 1995).

$$x = \sqrt{\frac{2D}{a} \cdot (c_1 - c_2)} \cdot \sqrt{t} = A\sqrt{t} \qquad [1.7]$$

where:

x = depth of carbonation at time t, m
D = diffusion coefficient of CO_2 in (carbonated) concrete, m^2/s
a = necessary amount of CO_2 for the carbonation of the alkaline components, g/m^3
c_1 = CO_2 concentration of the surrounding air, g/m^3
c_2 = CO_2 concentration at the carbonation front, g/m^3
t = time, s
A = carbonation constant

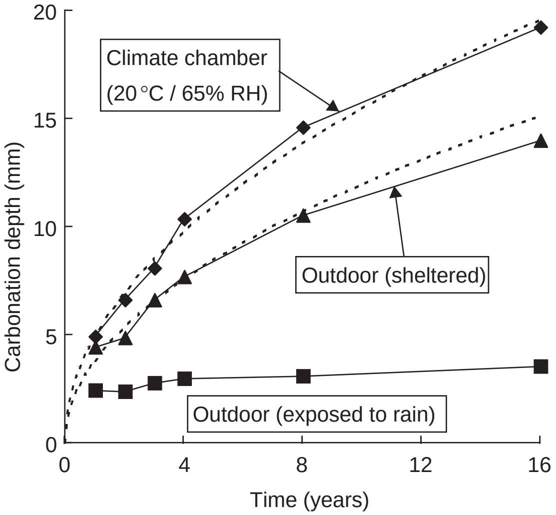
For the derivation of this equation several assumptions are necessary that are only valid for constant climatic conditions; such conditions are usually found only indoors or where concrete elements are protected from rain (Schröder et al. 1967, Schiessl 1976, Kropp and Hilsdorf 1995). Under outdoor conditions the progress of carbonation slows down continuously until it reaches a final value (Fig. 1.19).

In the mid-1970s Martin et al. (1975) and Schiessl (1976) presented a modified model taking into account the influence of the moisture content of the concrete on the diffusion coefficient of CO_2 and the back diffusion of $Ca(OH)_2$. With this extended $\sqrt{t}$-law they ended up with the conclusion that there was a final carbonation depth given in the following equation (Kropp and Hilsdorf 1995):

$$t = -\frac{a}{b}\left[x - x_\infty \cdot \ln\left(1 - \frac{x}{x_\infty}\right)\right] \qquad [1.8]$$

where:

x = carbonation depth at time t
x_∞ = final carbonation depth
a = necessary amount of CO_2 for the carbonation of the alkaline components (details given in Schiessl 1976)



1.19 Carbonation depth as a function of time. Dotted line: curve for the √t-law. Data from Wierig (1984).

b = constant depending on the moisture content, which describes the decrease of diffusion coefficient of CO_2 as well as the need for CO_2 caused by the back diffusion of the alkaline components (details in Schiessl 1976)

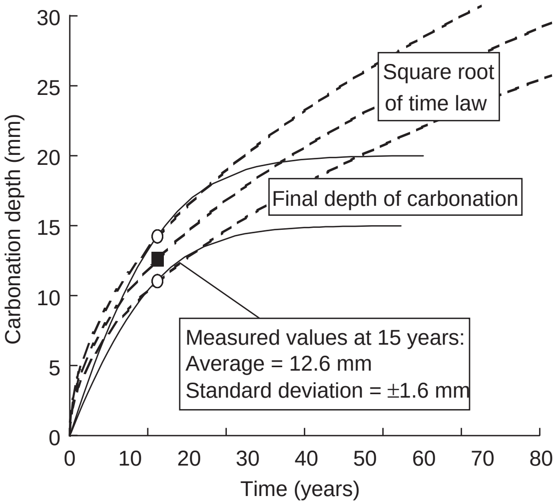
t = time

The use of the simple √t-law may lead to an unreasonable overestimation of the extrapolated carbonation depths as shown in Fig. 1.20. This may lead to unnecessary and uneconomical rehabilitation of a concrete structure.

1.6.5 Cracking of the concrete cover due to carbonation

The corrosion products of steel in carbonated concrete (e.g. rust) occupy a greater volume than does the original, non-corroded metal. This leads to a pressure build up around the steel rebars, then to visible cracks and finally to spalling of the concrete above the steel rebars.

There are a few quantitative results available on the effect of corrosion on cracking and spalling of the concrete cover; such results all show that the admissible mass loss and reduction of the cross-section respectively that lead to cracking are very small. The effect depends primarily on the diameter of the steel rebars, on the length of the corroding section of the rebar and on the thickness of the concrete cover. At a concrete cover to steel diameter ratio of 2 (e.g. concrete cover of 20 mm and a steel bar diam-



1.20 Extrapolation of the carbonation progress based on the simple and extended $\sqrt{t}$-law (Equations 1.7 and 1.8, respectively). The carbonation depth at 15 years has been determined for a reinforced concrete silo with Portland cement concrete of medium quality.

eter of 10 mm) cracking may already occur when the corroded metal layer is only 70 µm or less as can be seen in Fig. 1.21. With an increasing mass loss the crack width increases. The corrosion risk due to carbonation of concrete depends on the carbonation depth in relation to the cover (Parrott 1990). This is illustrated in Table 1.5.

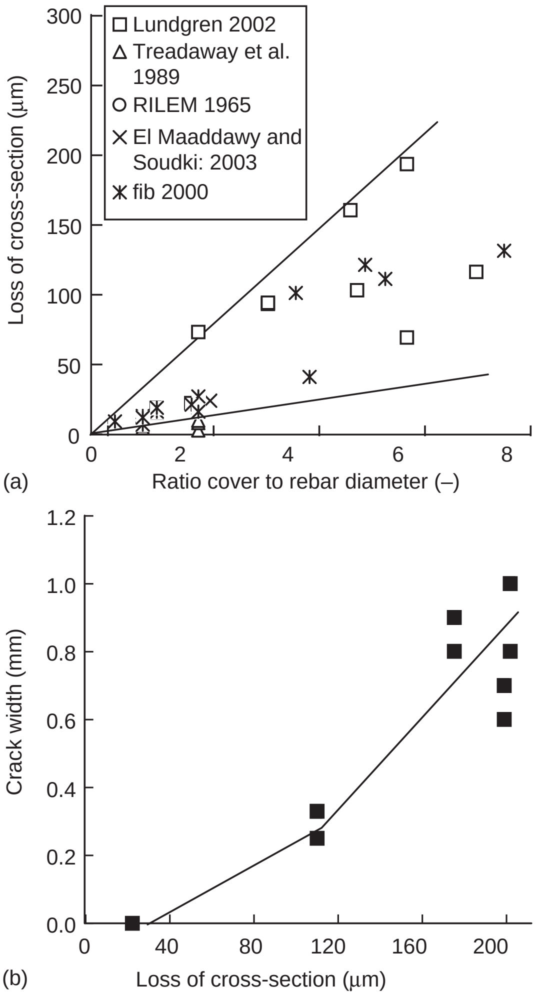
1.7 Chloride-induced corrosion

1.7.1 Chloride ingress

The fastest ingress of chloride into concrete is caused by capillary suction of chloride-containing water (e.g. sea water, water with dissolved deicing salts, chloride-containing floors, e.g. magnesia floors), which results in more or less deep chloride profiles (Fig. 1.22). Wetting and drying of the concrete accelerates the chloride ingress.

1.7.2 Negative effects of chlorides

The chloride has a fourfold negative effect in reinforced concrete (Hunkeler 1994):



1.21 (a) Relation between loss of cross-section for crack initiation and ratio of concrete cover to steel rebar diameter. Data from RILEM (1965), Treadaway et al. (1989), fib (2000), Lundgren (2002), El Maaddawy and Soudki (2003); (b) Relation between loss of cross-section and crack. Data from El Maaddawy and Soudki (2003).

- It destroys the passive film of the steel rebar and makes corrosion attack possible.
- It reduces the pH of the pore water since it reduces the solubility of $Ca(OH)_2$.
- It increases the moisture content because of the hygroscopic properties of salts present in concrete (e.g. $CaCl_2$, NaCl).
- It increases the electrical conductivity of the concrete.

Table 1.5 Corrosion risk due to carbonation of concrete based on Parrott (1990)

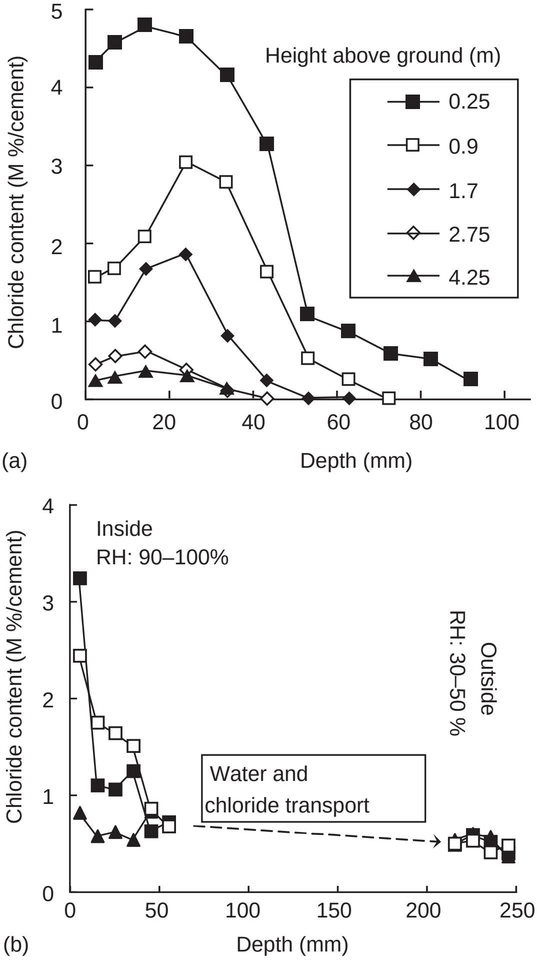
Carbonation depth/ Cover thickness d_{Carb}/d_{Cov}	Concrete condition	Rebar condition	Corrosion risk
<0.5	not cracked	not corroded	none
>0.5	not cracked	not corroded	small
~1.0	minor cracks	minor corrosion	increased
>1.0	cracked, minor spalling/ delamination	significant corrosion	serious
»1.0	cracked, major spalling/ delamination	loss of area	critical

1.7.3 Free and bound chloride

Not all of the chlorides in concrete are mobile and thus available for initiating or enhancing corrosion. A part of the chlorides is bound to the cement matrix, especially to the aluminates. The binding capacity depends on the type of cement and mineral additions (Fig. 1.23). However, this binding of the cement matrix is not permanent and the chlorides may be released again, e.g. if the pH is further reduced by ongoing carbonation. The correct analysis of the chloride content in concrete has led to research work (Hunkeler et al. 2000). Correct values are important for the assessment and repair of reinforced concrete structures and there is now a draft European standard for the chemical determination of the chloride content of hardened concrete (CEN 2003).

1.7.4 Critical chloride content for corrosion

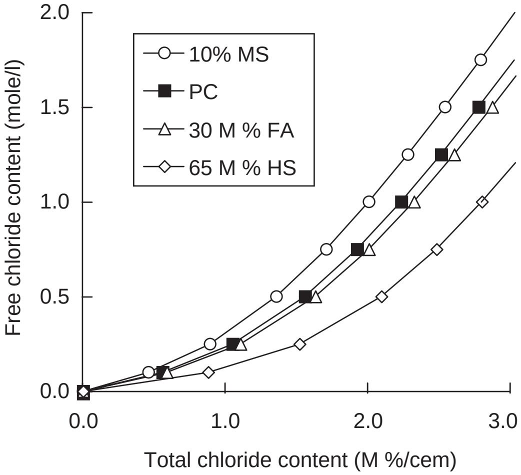
It is commonly known that at higher chloride content in concrete, chloride-induced corrosion or pitting corrosion of the steel rebars may occur. It is also accepted that the chloride level has to exceed a threshold value at the rebar surface to initiate the corrosion process. Earlier research work suggested a critical value of 0.4% chloride by mass of cement (Richartz 1969) or a critical chloride/hydroxyl ion ratio 0.6 (Hunkeler 1994, Breit 1997a). Since the pH of concrete varies according to the composition of concrete (e.g. type of cement, w/c ratio) and in the concrete cover with the carbonation (Hunkeler 1994, Broomfield 1997) a fixed or single value for this threshold cannot be expected.



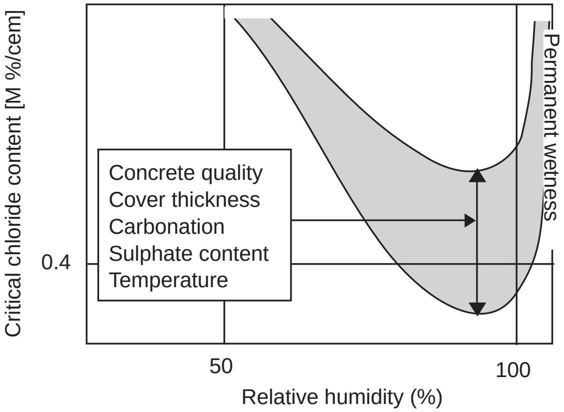
1.22 (a) Chloride profiles of backwall of a gallery for the traffic exposed to deicing salt water (Hunkeler 1994); (b) Chloride profiles of a free-standing wall of a swimming pool filled with salt water (Hunkeler 1994).

The critical threshold depends on various factors such as concrete quality (e.g. chloride-binding capacity), moisture content, concrete cover (oxygen availability, pH) (Fig. 1.24, Table 1.6). The experiences in many countries show the following relation between the chloride content (by mass of cement) and the corrosion risk:

<0.2 M %	low corrosion risk
0.4 M %	small corrosion risk
>1.0 M %	high corrosion risk



1.23 Free chloride concentration as a function of the total chloride content of concrete for different types of cement. FA = fly ash; HS = ground granulated blast furnace slag; MS = silica fume; PC = ordinary Portland cement. Data from Glass et al. (1997).



1.24 Influences of the critical chloride content for chloride-induced corrosion (Hunkeler 1994).

Table 1.6 Influences on the critical chloride content (Hunkeler 1994)

Major influences	Further influences
moisture content of concrete pH of the pore water (depends on e.g. carbonation, type of cement, w/c) ratio chloride/hydroxyl ions chloride-binding capacity of cement concrete cover (O_2 availability)	type of cement content of other corrosion enhancing compounds (e.g. SO_4^{2-}) w/c ratio condition of the surface of the steel rebars before concreting temperature (usual range variation)

Finally it has to be pointed out that the initiation of the corrosion process is a statistical phenomenon since weak spots on the surface of the steel rebar and in the cement matrix as well as of the interface between them are randomly distributed. Different studies have shown that the probability of the initiation increases steadily with increasing chloride level (Breit 1997b, Zimmermann 2000).

1.7.5 Time laws for the chloride ingress

There are different equations to describe the time behaviour of the chloride ingress. Many authors have based their calculation on Fick's second law (e.g. Bamforth 1996, Tang 1996b, Siemens et al. 1998, Thomas and Bamforth 1999, Helland 2001).

$$c(x,t) = c_s\left[1 - \operatorname{erfc}\left(\frac{x}{2\sqrt{D_{eff,C} \cdot t}}\right)\right] \qquad [1.9]$$

where:

$c(x,t)$ = chloride content at depth x and time t, M %/cem.
erfc = error function,
$D_{eff,C}$ = effective chloride diffusion coefficient, m^2/s
c_s = surface or near surface chloride content, M %/cem.
x = depth, m
t = time (age), s

With this equation the chloride profiles can be calculated as a function of time and surface chloride concentration. It must be recognised that the chloride diffusion coefficient is not a constant but varies for instance with the age (time), depth (pore structure) and the moisture content of the concrete (climatic conditions). Additionally, the ingress of chloride is not a pure diffusion process as discussed above. While this calculation gives only a rough figure of the reality, it might be of some help in the design of reinforced concrete structures.

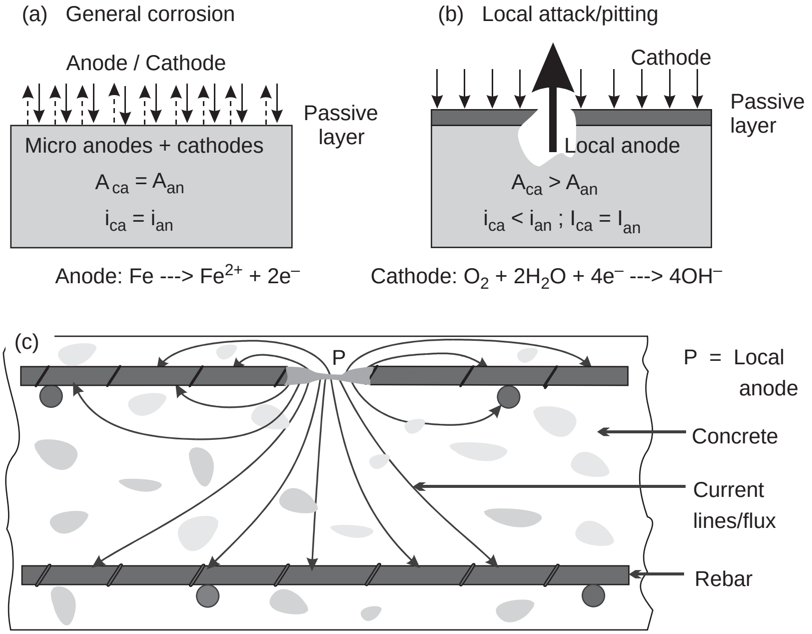
1.8 Corrosion rate

1.8.1 Macroelement

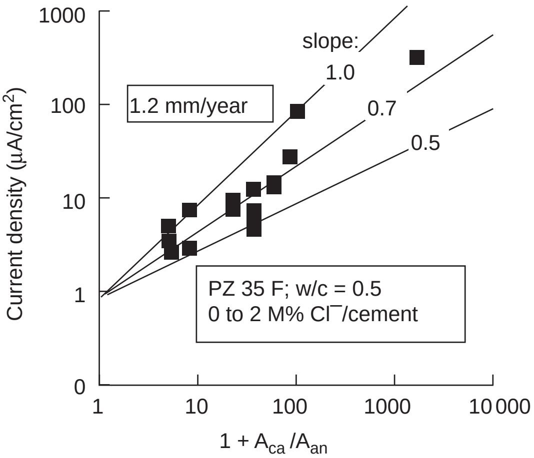
Corrosion initiated by pH lower than 11.5 or by chlorides leads to a localised attack of the steel rebars that are in the remaining part noncorroding, i.e. in the passive state (Hunkeler 1994). A macroelement is developed; this is a galvanic element between an anode (area of the local attack) and a cathode (noncorroding area) (Fig. 1.25). The effect of a macroelement can roughly be estimated by Equation 1.10, which takes the areas of the anode (A_{an}) and the cathode (A_{ca}) into account.

$$i_{corr} = i^0_{corr}\left(1 + \frac{A_{ca}}{A_{an}}\right) \qquad [1.10]$$

Compared to the value without any influence of a macroelement, i^0_{corr}, the corrosion rate i_{corr} is doubled according to this equation when the anode and cathode have the same dimensions. In practice, the area of the cathode is much larger than the area of the anode and thus for an area ratio of 100



1.25 (a) General corrosion; (b) Local attack (pitting corrosion) and (c) macroelement corrosion in concrete. A = Area; i = current density (e.g. mA/cm^2); I = current (e.g. mA).



1.26 Influence of the ratio A_{ca}/A_{an} on the corrosion rate i_{corr} according to Equation 1.10 (Hunkeler 1994). Data from Schiessl and Schwarzkopf (1986). PZ: Portland cement.

the i_{corr} increases by a factor of 101 at the maximum (Fig. 1.26). At high ratios of A_{ca}/A_{an} the increase of i_{corr} is below that expected. The reason for this deviation is caused by the electrochemical resistances of the anodic and cathodic reaction and these electrochemical resistances limit the current flux. Equation 1.11 allows a better estimation taking into account the driving force of the macroelement ΔU (= potential difference between the anode and the cathode) and the electrochemical resistances (Hunkeler 1994).

$$i_{corr} = \frac{I_{corr}}{A_{an}} = \left(\frac{\Delta U}{R_{an} + R_{ca} + R_E}\right)\frac{1}{A_{an}} = \frac{U_{corr,ca} - U_{corr,an}}{r_{an} + \frac{r_{ca}A_{an}}{A_{ca}} + \frac{\rho_c A_{an}}{L}} \qquad [1.11]$$

where

I_{corr} = corrosion current, A
i_{corr} = corrosion current density, A/m^2
ΔU = driving force (= difference of the corrosion potentials), V
R_{an} = resistance of the anode, Ω
R_{ca} = resistance of the cathode, Ω
R_E = electrolyte, concrete or ohmic resistance, Ω
$U_{corr,an}$ = corrosion potential of the anode, V
$U_{corr,ca}$ = corrosion potential of the cathode, V

A_{an} = area of the anode, m^2
A_{ca} = area of the cathode, m^2
r_{an} = specific electrochemical resistance of the anode, $\Omega\ m^2$
r_{ca} = specific electrochemical resistance of the cathode, $\Omega\ m^2$
ρ_C = specific electrical resistance or resistivity of the concrete, Ω m
L = characteristic length, m

For a given macroelement the parameter L is a characteristic length and depends on the concrete volume around the rebar (cover thickness), on the anodic and cathodic area as well as on the distance between anode and cathode (current path) and on the concrete resistivity. The parameters in Equation 1.11 are partly dependent on each other; for instance the electrochemical resistances depend on the current density, the driving force of the macroelement and the cathodic area on the concrete resistivity. In very well-defined laboratory experiments it is possible to determine the influence of the different parameters and from such experiments the following conclusions were drawn (Hunkeler 1994):

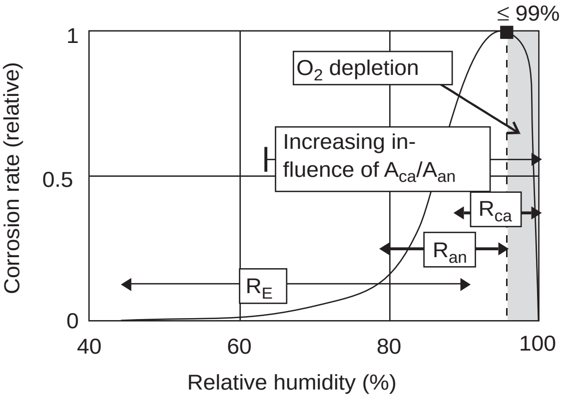
- The driving force ΔU decreases with decreasing moisture content of the concrete (= increasing concrete resistivity).
- The electrochemical resistances (r_{an}, r_{ca}) as well as the ohmic resistance increase with decreasing moisture content. The cathodic charge transfer resistance r_{ca} grows faster with decreasing moisture content than does r_{an}. In wet concrete the ratio r_{an}/r_{ca} is around 10, in dry concrete >100.
- The cathodic area of the macroelement increases with decreasing moisture content.
- The anodic charge transfer resistance r_{an} depends on the size of the anode and becomes smaller with increasing area of the anode.
- The galvanic current of the macroelement increases with:
  - increasing moisture content of the concrete (decreasing resistances);
  - increasing area of the corroding site if the ratio A_{an}/A_{ca} remains constant;
  - increasing ratio A_{an}/A_{ca} (up to a maximum which depends mainly on r_{an} and on the moisture of the concrete);
  - increasing temperature.

From Equation 1.11 three limiting cases might be deduced:

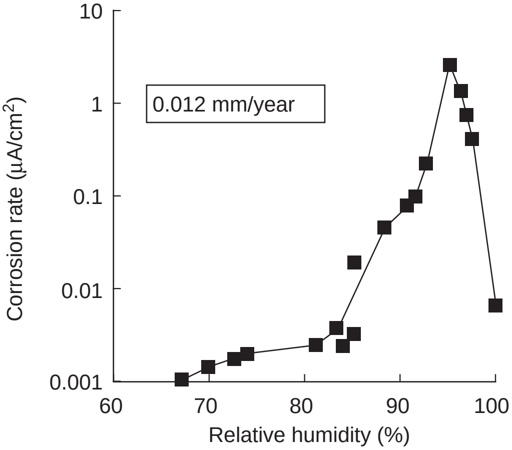
Case 1: anodic control $R_{an} \gg R_{ca}, R_E$
Case 2: cathodic control $R_{ca} \gg R_{an}, R_E$
Case 3: ohmic control $R_E \gg R_{ca}, R_{an}$

1.8.2 Influence of the relative humidity

In real systems the above mentioned limiting cases do not occur in pure form. With the exceptions of very dry or permanently wet concrete with oxygen depletion usually two factors at least determine the corrosion rate. These complex interactions are schematically shown in Fig. 1.27. Results of laboratory experiments on carbonated reinforced concrete samples are given in Fig. 1.28.



1.27 Dependency of the corrosion rate on the water saturation and regions of dominant resistance (Hunkeler 1994).



1.28 Corrosion of steel in carbonated mortar (Hunkeler 1994). Data from Parrott (1990).

The position of maximum current density in respect to the relative humidity (RH) of the air (moisture content of the concrete) depends on R_{an} and on the ratio A_{ca}/A_{an}: the smaller R_{an} and the larger A_{ca}/A_{an} the higher is the maximum. Because of the dependency of the oxygen diffusion coefficient on the moisture content one can assume that the maximum is reached at RH values lower than 99%. For real concrete components the cathodic area may be in dry or moist concrete and the corroding area rather in the wet part of the concrete element. The oxygen depletion in the wet concrete therefore may not influence greatly the corrosion current density.

1.8.3 Concrete resistivity as reaction-controlling factor

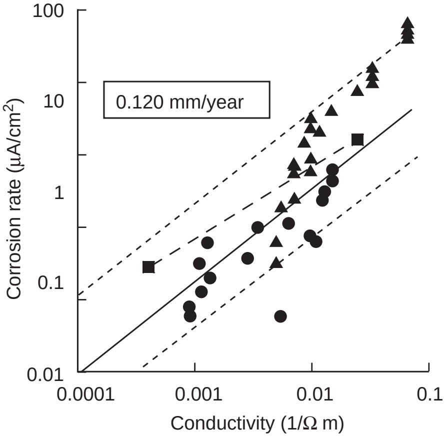
Under practical conditions it is not easy to determine the electrochemical resistances because the area of the anode and cathode are unknown and cannot be measured by direct means without destruction of the concrete. In some cases a simplification is possible and the electrochemical resistances may be neglected, e.g. at low moisture content of the concrete. At lower RH values, i.e. at lower moisture content of the concrete, the electrolyte resistance R_E and the resistivity ρ_C are the governing factors of the corrosion process (limiting case 3). In this case the corrosion current density i_{Corr} is approximately inversely proportional to the electrolyte resistance R_E and resistivity ρ_C, or directly proportional to the conductivity σ_C according to Equation 1.12.

$$i_{corr} \approx \frac{1}{R_E} \sim \frac{1}{\rho_C} = \sigma_C \qquad [1.12]$$

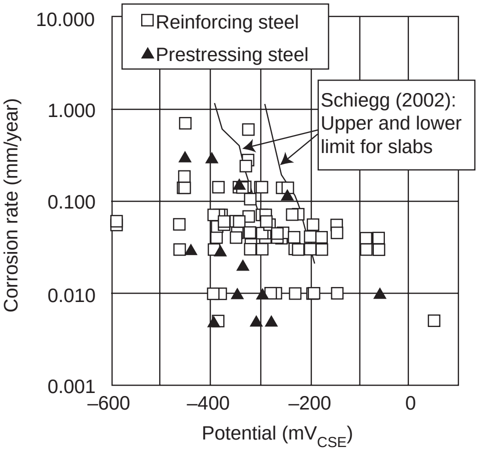
The results of different studies were analysed by Hunkeler (1994) and are shown in Fig. 1.29. Although the scatter is obviously large this type of information may be of great help in practice where one has to determine the corrosion risk and the corrosion rate as well as to judge the effect or efficiency of repair methods, for instance after the application of coatings on concrete surfaces. Although the importance of the resistivity is generally accepted there have been only a small number of systematic and long-term studies on the resistivity of concrete and, specifically, its dependence on the relative humidity.

1.8.4 Potential dependency of the corrosion rate

The corrosion potential of the reinforcement decreases with increasing chloride level or decreasing pH at the surface of steel rebars. This dependency is used with the potential mapping technique to find concrete areas with corroding steel rebars. A decreasing corrosion potential is a sign of corrosion; in general, the lower the potential the higher the corrosion rate. Figure 1.30 shows the results of an extensive investigation of chloride-contaminated post-tensioned girders of a bridge in Switzerland. The corrosion rate was calculated based on pit depths measured on excavated



1.29 Corrosion rate as a function of the conductivity of concrete (Hunkeler 1994). Data from Nöggerath (1990), Raupach (1992), Tondi et al. (1993).



1.30 Corrosion rate of the reinforcement in chloride-contaminated and carbonated concrete of girders of a bridge as a function of the potential. The corrosion rate of the reinforcing and prestressing steel was calculated from the loss of cross-section measured after removal of the concrete cover. The lines represent the upper and lower limit for slabs and of exposed concrete components of Swiss bridges found during long-term monitoring (Schiegg 2002).

steel rebars. This figure contains the limits found for different components of Swiss bridges (e.g. decks, columns).

From Fig. 1.30 the following can be seen:

- At very negative potentials corrosion rates above 1 mm/year are possible.
- Prestressing steel with a higher concrete cover than ordinary reinforcing steel shows much lower corrosion rates.
- The corrosion rate increases steeply at potentials below –250 mV_{CSE}.
- At a potential of –225 mV_{CSE} the border line for the bridge changes the slope and it is less steep at potentials above –225 mV_{CSE}. This might be caused by the preceding rehabilitation or by corrosion due to the carbonation of concrete.

1.8.5 Influence of temperature

The resistivity of concrete and, therefore, the corrosion rate depends strongly on the temperature (Fig. 1.29). The resistivity approaches zero by rather low temperatures around –25 to –40 °C. It can be described by Equation 1.13 (Hunkeler 1994).

$$\rho_C = \rho_{C,0} e^{b_\rho\left(\frac{1}{T} - \frac{1}{T_0}\right)} \qquad [1.13]$$

where

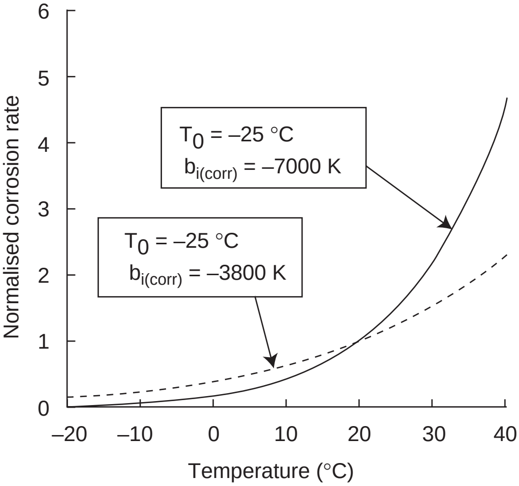
$\rho_{C,0}$ = resistivity at T_0 (T_0 appr. between –25 and –40 °C)
T, T_0 = absolute temperature in K
b_ρ = constant in K
For b_ρ values between 2100 and 5500 K have been found (Hunkeler 1994, Schiegg 2002).

The corrosion rate increases with increasing temperature. This holds true for corrosion caused by carbonated concrete as well as for the chloride-induced attack. The temperature dependency of the corrosion rate is given by Equation 1.14.

$$i_{corr} = i_0 e^{b_{i,corr}\left(\frac{1}{T} - \frac{1}{T_0}\right)} \qquad [1.14]$$

where

$I_0 = i_{corr}$ with T_0 (T_0 approximately between –25 and –40 °C)
T, T_0 = absolute temperature in K
$b_{i,corr}$ = constant in K.



1.31 Influence of the temperature on the corrosion rate (normalised to 20 °C) (Hunkeler 1994).

For the constant $b_{i,corr}$ values between 3800 and 7000 K have been found (Hunkeler 1994, Schiegg 2002). These values are slightly higher than those for the resistivity. The influence of the temperature on the corrosion rate is, therefore, slightly stronger than on the resistivity. Figure 1.31 shows graphically this influence. It can be seen that the corrosion rate varies by more than a factor of ten in a common seasonal temperature range from – 5 to 30 °C.

1.9 General aspects of corrosion prevention

1.9.1 General considerations

Many reinforced concrete structures show signs of deterioration even when young and have to be rehabilitated which involves high financial costs and technical effort. The problem of corrosion due to carbonation of concrete is solved. National standards make provisions for concrete cover and the properties of concrete and an appropriate dense concrete and concrete cover guarantee a long life. In contrast to this there is no established consensus on the most economical and technically feasible steps that can be taken against chloride-induced corrosion attack. Durability design offers different methods and protection possibilities.

Generally, not only the cost of the construction but also the cost of maintenance and rehabilitation must be considered (life-cycle costs, LCC). For construction where the aim is to have low or almost zero maintenance costs (‘zero maintenance strategy’) different possibilities may improve the resistance of the construction against deterioration processes (Table 1.7). Improving the concrete quality and increasing the concrete cover are by far the most economical protection measures but are not always enough. Practical experience with epoxy-coated reinforcement gives contradictory results (Richner and Kürsteiner 2001). The same holds true for the application of inhibitors (Hunkeler et al. 2001).

1.9.2 Improving the chloride resistance of concrete

The resistance of concrete against chloride ions penetrating (chloride ingress) from the outside, the so-called chloride resistance, can be improved by reducing the water to cement and water to binder ratio, respectively, or by using mineral additions, e.g. fly ash, silica fume, ground granulated blast furnace slag (ggbs) or metakaolin (Fig. 1.32). These figures show the results of a literature review and an extensive research study with a variety of laboratory concretes and concrete samples taken from 20 to 40 year old Swiss reinforced concrete structures. In this figure the results of other research work (Tang 1996a, Tang 1996b, Gehlen 2000, Mackechnie and Alexander 2000) have been included.

1.9.3 Improving the corrosion resistance of the reinforcement

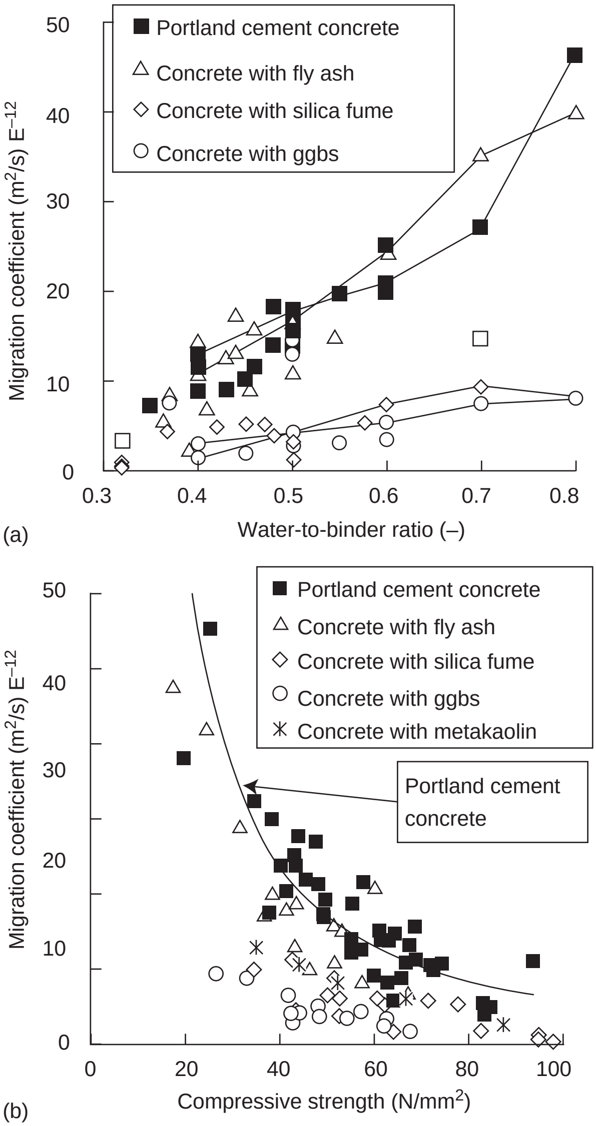
The use of stainless steels is one of the most promising measures that can be taken to prevent premature failure. Stainless steels exhibit a much higher corrosion resistance than ordinary black, zinc or epoxy-coated rebars. Although the material costs are higher they may be used as an appropriate additional measure for the protection of concrete components with a high risk of corrosion (Hunkeler 2000, Hunkeler 2001). Table 1.8 gives some information for practical applications.

Table 1.7 Overview and comparison of some additional protection measures for durable reinforced concrete structures (Hunkeler 2000, Hunkeler et al. 2001)

Measure	Advantage	Disadvantage
Increase the concrete cover of the reinforcement	costs handling (easy to realise) experience eventually higher critical chloride content for corrosion	there are limits for the increase reduces the static height
Use of more tight (less porous) concrete	costs handling (partly) experience (partly)	there are limits for the reduction of the w/c ratio (↔ workability) concrete remains – even at very low w/c ratios – a porous material low w/c ratios and the addition of mineral additions (e.g. silica fume, fly ash or ground granulated blast furnace slag) may not or may only slightly change the critical chloride content for corrosion; some mineral additions may even reduce it.
Inhibitors as admixture for concrete	handling eventually a higher critical chloride content for corrosion	costs long-term efficiency and durability not proven
Surface protection systems (e.g. hydrophobic impregnation, coatings, tiles)	positive effect (if the correct system has been chosen and correctly applied) a large variety of systems available appearance of the surface (colours) can be modified	costs handling, susceptibility to damages during work the efficiency has to be monitored needs maintenance and repair modification of the appearance of the concrete surface (loss of the character of fair-faced concrete)
Zinc-coated steel	costs handling performance in carbonated concrete	limited efficiency and durability in highly chloride-contaminated concrete and in cracks no or only a slight influence on the critical chloride content

Table 1.7 Continued

Measure	Advantage	Disadvantage
Epoxy-coated steel	costs deliverability	handling on construction sites, susceptibility to damages during work mixture between coated and ordinary (non-coated) reinforcement critical long term efficiency and durability not proven (delamination of the coating and corrosion underneath the coating), contradictory experiences no or only a slight influence on the critical chloride content
Stainless steel	handling higher critical chloride content for corrosion (dependent on the steel quality) mixture between stainless and ordinary reinforcement without any restrictions or additional measures possible	costs restricted deliverability, availability, delivery forms, deadlines and amount of delivery experience
Cathodic protection	efficiency	costs handling ('complicated') monitoring necessary
Waterproofing membranes	efficiency experience	costs handling (risk of damages) not always applicable



1.32 (a) Relation between chloride migration coefficient (= measure of the resistance of concrete against chloride ingress) and water-to-binder ratio (Hunkeler et al. 2002); (b) Relation between chloride migration coefficient and compressive strength and influence of mineral additions. The regression curve for Portland cement concrete was calculated based on results on young laboratory concrete and on concrete cores taken from 20 to 40 years old reinforced concrete structures; ggbs = ground granulated blast furnace slag (Hunkeler et al. 2002).

Table 1.8 Survey of the use of stainless steel rebars for concrete structures exposed to chloride-containing environments and with a concrete cover of the rebars of about 30 mm, compared with other rebar materials (Hunkeler 2000, Hunkeler 2001). CRC = corrosion resistance class; PRE = pitting resistance equivalent; classification: + appropriate, – inappropriate; classification in parenthesis: classification uncertain

Rebar material	PRE[1]	CRC			Carbonated concrete			
			no	yes	no	yes	[yes][2]	[yes][2]
					Chloride content[3]			
			zero	zero	low	low	mid	high
Ordinary black steel rebar	0	0	+	–	+/–	(–)	–	–
Epoxy-coated steel rebar[4]	0	?						
Zinc-coated steel rebar	0	0/1	+	+	(+)	–	–	–
Chromium steels[5]	10–16	1	+	+	+	(+/–)	(+/–)	–
Chromium–nickel steels and chromium–nickel–molybdenum steels	17–22	2	+	+	+	+	+	(+)
Chromium–nickel–molybdenum steels	23–30	3	+	+	+	+	+	+
Chromium–nickel–molybdenum steels[6]	>31	4						

[1] PRE: Pitting resistance equivalent. PRE = %Cr + 3.3%Mo + 0%N.
The minimum content of chromium and molybdenum according to EN 10088 and Stahlschlüssel (Germany) was used for the calculation. The nitrogen content was not taken into account.

[2] The influence of the chloride content dominates. Carbonation is of minor importance since the rate of carbonation is low or the concrete cover is high.

[3] Chloride content: low: ≤0.6 M % by mass of cement
middle: ≥0.6, but ≤1.5 M % by mass of cement
high: ≥1.5, but ≤5 M % by mass of cement
very high: >5 M % by mass of cement

[4] The classification is uncertain/controversial.

[5] The susceptibility to pitting corrosion of chromium-steels with a low chromium content increases rapidly with decreasing pH. Depending on the concrete cover the carbonation of the concrete is, therefore, more or less important.

[6] For special cases e.g.:
- very high chloride content.
- high chloride content and further unfavourable circumstances.

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2

Monitoring of corrosion in reinforced concrete structures

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2.1 Introduction

Corrosion of rebars in reinforced concrete structures is a complex process that is strongly influenced by the interaction of the exposure conditions with the concrete. From the experience of condition surveys on reinforced concrete bridges it is known that the exposure of a structure has a decisive influence on the location and extent of corroding rebars. However, in most cases it is difficult to quantify its influence on past and future corrosion propagation.

In the last 15 years the goal of repair work was to stop or at least strongly decrease the ongoing corrosion processes and to protect concrete against the penetration of water and pollutants e.g. chlorides. In this period the methods of condition survey and data evaluation were constantly improved. However, there was clearly less attention paid to the corrosion monitoring of new and repaired structures and, as a consequence, there are only few methods and little experience available in this field today.

In this chapter the goals and different methods for the monitoring of reinforced concrete structures are presented. These methods can be used for new, existing or repaired structures. Often the situation is more complex after repair work on a structure, because this can involve different products and interfaces, than on a new or existing structure. Furthermore, the installation of different kinds of sensor elements is much easier for new structures. In addition, the state of the art sensor-based monitoring system is presented that allows the important parameters of the corrosion process to be measured. The instrumentation consists of chloride and resistance sensors as well as isolated corroding rebars that are mounted into drill cores from real structures or cores produced in the laboratory. The cores equipped with sensors are cast into structures with different exposure conditions. A data acquisition system was used for the continuous recording (measuring interval ≥ 1 minute) of concrete resistivity, potential, macrocell current and climatic parameters such as temperature and relative humidity.

2.2 Goals

There are various goals for the monitoring of corrosion in reinforced concrete structures. They depend on the state of the structure and on the measures taken to protect it.

- New structures
  - time of corrosion initiation;
  - causes of corrosion (chloride concentration, pH value, concrete humidity).
- Repaired structures
  - effectiveness and durability of repair work;
  - experience with specific repair methods or products;
  - causes of corrosion (chloride concentration, pH value, concrete humidity).
- Existing structures
  - corrosion rate;
  - causes of corrosion (chloride concentration, pH value, concrete humidity).

In addition, indirect information for the evaluation of the corrosion risk can be gained. Corrosion protection measures such as inhibitor treatment or hydrophobic treatment can readily be characterised regarding its efficiency and durability, e.g. the effectiveness of a surface protection can be investigated. A proper water-rejecting hydrophobic treatment reduces the water absorption, which leads to a low concrete humidity. Whether this impregnation is capable of reducing the corrosion rate sufficiently cannot be answered without additional information.

Often quantitative results (e.g. corrosion rate) are not readily available for concrete. Nevertheless, in many cases the knowledge of relative changes of important parameters is sufficient to make a reasonable evaluation of a corrosion propagation trend. A pronounced increase of concrete humidity in a bridge deck can be related to leakages of the sealing or an increase of the corrosion current will show the reinitiation of corrosion attacks.

The type of a monitoring system and the parameters investigated depend on the following factors:

- Importance of a structure (statics, aesthetics, accessibility).
- Cause of corrosion (chlorides, carbonation).
- Readiness of the owner to install a monitoring system, costs.

Only limited information is available on the monitoring of corrosion in reinforced concrete structures. This is also true for many repair methods, especially regarding their durability. Basic questions about corrosion mechanisms of steel in concrete must be answered and for this reason an increasing number of monitoring applications should be considered. This in turn leads to new findings on durability of reinforced concrete structures.

2.3 Types of monitoring techniques

With the different methods for corrosion monitoring one can differentiate between cover-all and local measurements. Local information can be derived from the following:

- Built-in the structure (sensors, reference electrodes).
- Mobile structures, but these however are not suitable for cover-all measurement (high duration for one measurement, not non-destructive).

In Table 2.1 the most important methods are shown. In the following sections some applications are explained in more detail.

Table 2.1 Overview of the most important methods for corrosion monitoring

Parameter	Method	Application
Corrosion rate	Polarisation resistance linear polarisation resistance (LPR) impedance spectroscopy (EIS) galvanostatic pulse measurement (GPM)	Mobile/local
Macrocell current	Artificial anodes insulated rebars macrocells	Fix/local
Potential	permanent reference electrode	Mobile
	movable reference electrodes	Fix/local
Concrete resistivity	4-electrode-resistivity measurement	Mobile
	insulated rebars	Fix/local
	instrumented cores	Fix/local
	multi-ring electrode	Fix/local
Chloride concentration	chloride analysis of concrete cores	Mobile/local
	chloride sensors	Fix/local
Carbonation depth	phenolphthalein test	Mobile/local
	potential profiles	Mobile/local
Auxiliary parameters		
air and concrete temperature	temperature sensors	Fix/local
relative humidity	humidity sensors	Fix/local

2.3.1 Corrosion rate

The measurement of the polarisation resistance R_p by means of electrochemical methods allows calculation of the corrosion rate according to Equation 2.1.

$$\frac{1}{R_P} = \frac{i_{corr}}{B} \qquad [2.1]$$

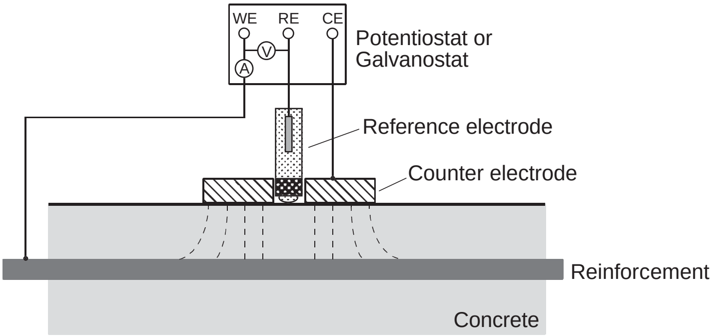
where:

R_p = polarisation resistance [$\Omega^{-1}\,cm^{-2}$]
i_{corr} = corrosion current density [$\mu A\,cm^{-2}$]
B = system constant [V]

The reciprocal polarisation resistance is the slope of the current density–potential curve in the proximity of the corrosion potential[1]. The system constant B contains the kinetics of the anodic and cathodic reaction and amounts to 26 mV for corroding steel and 52 mV for passive steel in concrete[2]. The polarisation resistance can be determined by the following methods. All these methods have a similar measuring set-up with counter and reference electrodes on the concrete surface (Fig. 2.1).

2.3.1.1 Linear polarisation resistance

In linear polarisation resistance measurements (LPR) a constant potential ξ ($\xi = \xi_{corr} \pm 5$ mV and ± 10 mV) is applied to the steel in the concrete. After some minutes (stationary conditions) the resulting current is measured. The effective polarisation resistance $R_{p,eff}$ must be compensated by the ohmic resistance of the concrete, which can be determined by an impedance measurement.



2.1 Schematic set-up for electrochemical measurements on reinforced concrete structures.

2.3.1.2 Electrochemical impedance spectroscopy

The measurement set-up of electrochemical impedance spectroscopy (EIS) is similar to that of LPR. An AC voltage signal in a frequency range from several MHz to approximately 100 kHz is applied and the resulting AC current is measured. By analysing the impedance spectrum the ohmic resistance of the concrete or the polarisation resistance can be determined. A disadvantage of this method is the time exposure for one measurement, depending upon the lowest frequency and therefore EIS is barely applied on real structures.

2.3.1.3 Galvanostatic pulse measurement

Galvanostatic pulse measurement (GPM) is the most efficient method for the determination of the polarisation resistance R_p (length of time per measurement approximately 10 seconds). A galvanostatic current is applied to the reinforcement and the polarisation is recorded by a computer. The current of the pulse is selected in such a way that the change of the corrosion potential is less than 20 mV. By curve fitting and extrapolation of time towards infinity the ohmic resistance of the concrete and the polarisation resistance R_p can be calculated.

2.3.1.4 Results and experience

In laboratory investigations a good agreement of the results of the methods described with the actual corrosion rate was found if the measured results were compensated by the ohmic resistance of the concrete[3]. For an estimation of the corrosion rate in real structures the geometry-independent specific polarisation resistance R^* has to be determined since the measured polarisation resistance depends on both the ohmic resistance of the concrete and the effectively polarised reinforcement surface. The current spread is dependent on:

- Corrosion state of the reinforcement.
- Concrete cover.
- Concrete resistivity.
- Diameter and distance of the rebars.
- Diameter of the counter electrode.

From the literature[3,4] it can be stated that in the case of homogeneously active reinforcement the current is concentrated below the counter electrode and no current spread occurs. Hence the determination of R^* is comparatively easy. However, passive steel has a very high polarisation resistance, which leads to a pronounced current spread. The distance of the current spread can be estimated by L_{crit} from computer simulations. L_{crit} is defined as the distance from the edge of the counter electrode up to a current spread of 95 % and the major difficulty concerning L_{crit} is the fact that the corrosion state of the reinforcement has to be known. The wide current spread with passive reinforcement can be limited by using a guard ring[5].

In the case of chloride-induced corrosion the current is concentrated on the anodic area. This leads to an underestimation of the concrete resistance and an overestimation of the polarisation resistance (too small corrosion rates). The practical application of R_p measurements is appropriate for the investigation of relative changes over time. It can be used, in conjunction with other methods (e.g. potential field measurements), for monitoring of reinforced concrete structures. However, the interpretation of the data has to be handled with care where there may be significant changes of exposure conditions or concrete humidity.

2.3.2 Macrocell currents

Since the anode and cathode are geometrically separated in macrocell corrosion it is possible to measure the macrocell current by isolating the anode and the cathode from each other and to estimate the mass loss of the rebar. Generally, the macrocell currents can be measured by installation of artificial anodes or by mechanical cutting of the rebar mat. In both cases the corrosion elements must be measured with the smallest possible disruption of the existing concrete in order to generate no unwanted effects that do not represent the investigated structure. This requires the use of small test samples and small openings and the macrocell current can be measured over an internal shunt of a voltmeter or a zero ampere meter. It is not always possible to separate the anode from the cathode completely and in such cases only a part of the macrocell current will be measured and the corrosion rate can be underestimated.

2.3.3 Potential mapping

In order to estimate the necessity of repair work it is necessary to know the exact place and the extent of corrosion attacks at the reinforcement. Corrosion sites must be identified rapidly, non-destructively and over the entire surface. Potential mapping is used during three stages of bridge maintenance:

- During inspection (basis for the repair concept).
- During repair work.
- After repair work (quality assurance, monitoring).

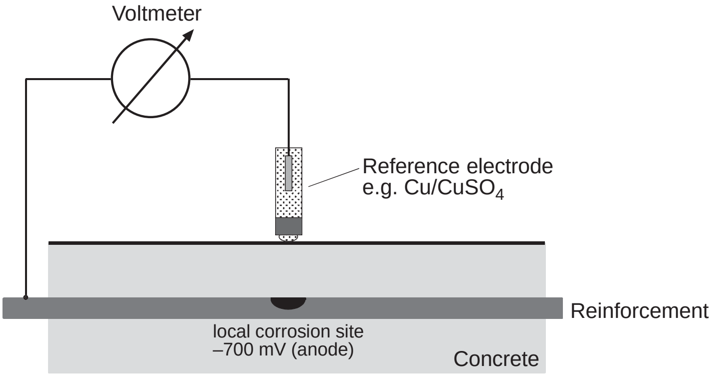
2.3.3.1 Principle and application

The principle of potential mapping is the potential difference of corroding and passive reinforcement. The corrosion potential of a corroding rebar in chloride-contaminated or carbonated concrete varies up to several 100 mVs from a non-corroding rebar in alkaline chloride-free concrete. The potential difference results in the macrocell current and the resulting potential drop in the concrete is measured. However, it has to be considered that besides the corrosion state the potential can be affected by other factors (e.g. concrete humidity, chloride content, pH value of the pore solution, stray currents), which lead occasionally to difficulties in the interpretation of the measured values. Potential mapping provides no information about the corrosion rate. Under certain conditions it is possible to estimate the corrosion rate on the basis of the potential gradients and the concrete resistivity[6].

The set-up for the measurements is shown in Fig. 2.2. Potential mapping requires a reference electrode with a well-known and constant potential, an electrical connection to the reinforcement and a voltmeter with a high input resistance. By placing the reference electrode on the concrete surface the resulting potential can be recorded. For easy evaluation of the data a colour code is used; during the evaluation a certain colour is assigned to the different potential values. This representation of the data permits a rapid determination of the extent of the corrosion attacks and can be used to determine the area of concrete removal.

2.3.3.2 Evaluation and interpretation of the potential readings

The correct evaluation of the data requires a knowledge of the corrosion of metals, in particular of the corrosion of steel in concrete. In addition to



2.2 Schematic set-up for potential mapping on reinforced concrete structures.

graphical illustration the potentials are statistically analysed and groups of corresponding values (e.g. active and passive zones) can be recognised. The statistical evaluation is a useful tool in specifying critical values for corrosion. More detailed explanations of the evaluation and the statistical analysis of the data are presented in the literature[7]. In addition to the statistical analysis of the data the results of visual inspection of rebars and chloride content in the concrete should be considered. It is important that the places for openings and drill cores are coordinated with the results of the potential measurement.

2.3.4 Concrete resistivity measurements

Concrete resistivity is an important parameter during corrosion processes and can be measured in various ways[8]. Measurements of concrete resistivity can be accomplished using DC or AC voltage. However, with DC voltage measurements polarisation effects at the electrodes have to be considered, which can falsify the results but this unfavourable influence can be eliminated e.g. by 4-point-measurements (see below). By use of AC voltage the polarisation potentials at the electrodes disappear. The impedance and the resulting phase shift depend on the frequency of the applied voltage. The measurement of impedance spectra can be used to characterise the dielectric behaviour of cementitious materials. Ideally, the measurements of concrete resistivity should be performed with frequencies within the range of 10 to 100 kHz.

2.3.4.1 Measurements using 4-electrode-resistivity

For the measurement of concrete resistivity at real structures, devices are used that are based on the 4-electrode-method, according to Wenner[9]. An AC-current is applied to the outside pair of electrodes and on the internal pair of electrodes the voltage drop is measured that leads to the electrical resistance. The advantage of this method is the elimination of possible electrode processes and the concrete resistivity can be determined from the surface. Information about concrete resistivity on different depths is achieved by the variation of the electrode gaps. Frequent difficulties of this method are the contacting of the electrodes on the concrete with wet sponges, the rebar mat, high impedance layers and an inhomogeneous moisture distribution in the concrete. In laboratory tests the four electrodes can be mounted into concrete samples (e.g. drill cores), which eliminates the disadvantages of the contacting on the concrete surface.

2.4 Sensors for concrete

Today the development and the use of sensor systems built into concrete for monitoring corrosion is increasing significantly. Based on the working principle sensor measurements can be differentiated into direct and indirect methods. Direct methods measure electrochemical parameters such as corrosion potential, macrocell current and polarisation resistance while indirect methods give information about the aggressiveness of the electrolyte or micro-cracking of the concrete due to corrosion processes (acoustic emission). Different sensors for corrosion monitoring listed in Table 2.2 are commercially available.

Artificial anodes are active corroding reinforcing bars that are embedded into a chloride-contaminated concrete or mortar. An electrical connection between the anode and the reinforcement mat of the structure is established to measure the macrocell current. It is recommended that the anodic rebar is weighed before installation so that the effective mass loss, depth of pitting holes and the anodic area can be determined at a later point of time. Such macrocell probes can be used in repaired or new structures. The use of artificial cathodes such as stainless steel or activated titanium is not recommended since the measurable currents are too small (the main part of the macrocell current flows into the extensive reinforcement mat) and no clear interpretation of the corrosion situation is possible.

A method without modification of the concrete properties around the anode is the use of insulated rebars. After localisation a corroding rebar is

Table 2.2 Sensors for corrosion monitoring

Direct methods	Sensor systems	Indirect methods	Sensor systems
Corrosion potential	Reference electrodes such as MnO_2	Concrete resistivity	Multi-ring electrode,
		Concrete humidity	Instrumented cores with resistivity sensors, humidity sensors, (artificial anodes, insulated rebars)
Macrocell current	Artificial anodes, artificial cathode, insulated rebars	Chloride concentration	Ag/AgCl chloride sensor, fibre optic sensors
Polarisation resistance	LPR-sensors	Acoustic emission	Local area monitoring system
Initiation of corrosion	Rebar probes, expansion-ring-anode, anode-ladder-system, anode-nail-system	Concrete humidity	Humidity sensors, concrete resistivity sensors
		pH value	Fibre optic sensors

cut near the crosses of the mat. On one end the electrical connection is made after removing a small amount of concrete and afterwards the opening is filled with a suitable mortar. A common problem of this technique is the precise localisation of the anodic spot which can be very time consuming.

The expansion ring-anode[10], anode-nail-system and anode-ladder-system[11] are monitoring systems that are used to determine the time of initiation when the critical chloride concentration is exceeded. If the steel sensors of the anode-ladder-system are connected to the lateral titanium bars the macrocell currents can also be measured. Due to the large dimension the anode-ladder-system is mainly suitable for new or repaired structures.

Microcracking of the concrete caused by corrosion processes can be recorded by acoustic emission measurements[12]. The local area monitoring system (LAM) is designed to monitor acoustic emission activities from defects on small areas of bridges.

AgCl-chloride sensors can be used to measure the ingress of chlorides into cement-based materials. In laboratory investigations the sensors work very well and give accurate results[13] and in field tests the chloride sensor combined with a reference electrode such as the MnO_2 electrode is a promising tool to determine the critical chloride concentration for corrosion initiation in concrete structures[14]. Experience from field tests shows that the sensors are particularly satisfactory in new structures. If there are already corroding areas present the potential measurement of the sensors can be strongly influenced by the electric field of the macrocell corrosion (potential shift) resulting in erroneous chloride concentrations[15]. The voltage drop cannot be quantified because it depends on the exact position of the sensors and the reference electrode and on the corrosion current variation in the structure.

Since concrete resistivity is related to it, the humidity in concrete is an important parameter in providing information on the corrosion risk. There are different sensor systems (e.g. multi-ring electrodes[16], instrumented cores) that allow monitoring the humidity exchange in the concrete cover by means of resistivity measurements.

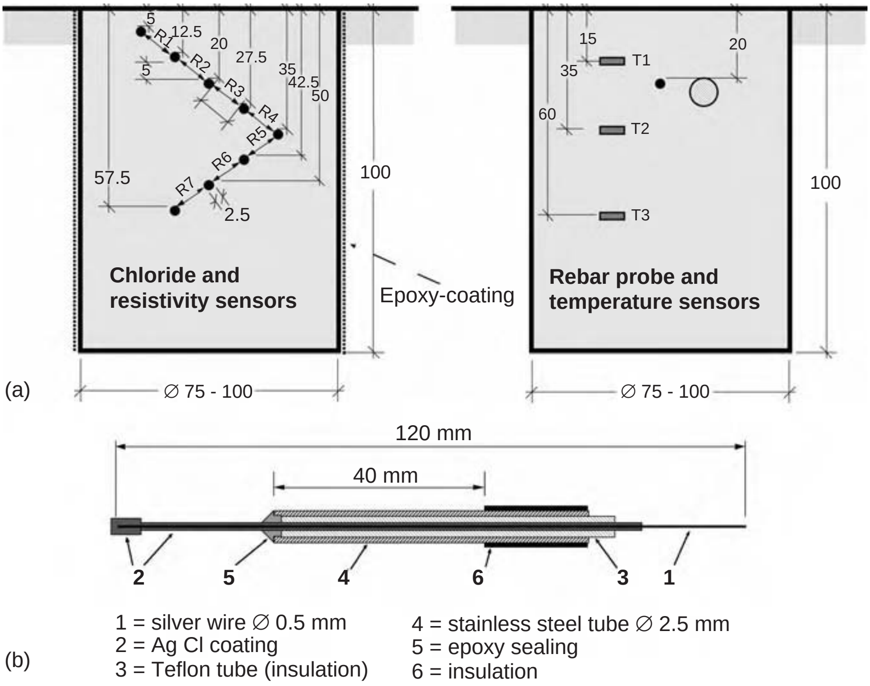
The perfect sensor does not exist for each sensor system has its advantages and disadvantages. The engineer or the owner of a concrete construction must study the goals of a planned monitoring system carefully and clarify what information is needed for the problem in hand.

2.5 Continuous method/online monitoring

The term online monitoring means the continuous measurement of certain parameters at real structures, where sensor devices are built into the concrete. By the use of short measuring intervals (minutes to hours) repeated in a systematic way, both temporary changes and long-term differences can be measured. To investigate the corrosion propagation, a new measuring technique has been developed, which allows important corrosion parameters to be measured directly at real structures[17].

2.5.1 Sensors and instrumentation

Investigations on corrosion propagation were based on the development of concrete cores equipped with sensors capable of monitoring the major parameters involved in the ongoing corrosion processes. In order to measure the moisture content and the chloride uptake as a function of the concrete depth, up to eight chloride and resistivity sensors are cast into cylindrical concrete samples (Fig. 2.3). The cores were taken from concrete structures or prepared in the laboratory. A further core contains a reinforcing bar (ordinary carbon steel, length 40 mm, Ø 8 mm) for corrosion current measurements, a chloride sensor as well as three PT1000 temperature sensors. The reinforcing bar can be removed later for further investigations. The lateral surfaces of the cores with the eight sensor elements are coated with



2.3 Instrumented cores for field tests. The following sensors were used: chloride and resistivity sensor (detail below the cores), rebar probe and temperature sensor.

an epoxy-resin coating in order to permit only one-dimensional water uptake perpendicular to the concrete surface. The instrumented cores are then fixed with a low viscosity mortar into boreholes at different locations on the concrete structure and the potentials of the chloride sensors are measured using an MnO_2-reference electrode embedded in the vicinity of the sensors. The cell factor of the resistivity sensors was determined in Na_2SO_4 solutions with different conductivities. Using instrumented drill cores and additional sensors for the registration of the climatic influences the following parameters can be measured:

- Electrical concrete resistance, R_C [Ω].
- Potential of the reinforcement, chloride sensor, U [$V(MnO_2)$].
- Corrosion current, I_{corr} [A].
- Air and concrete temperature, $T_{A/C}$ [°C].
- Relative humidity, rh [%].

The cores with the sensors were mounted in the boreholes of structures with different exposure conditions.

2.5.2 Data acquisition

A data acquisition system for the continuous recording (measuring interval ≥1 minute) of resistivity (concrete humidity), potential (corrosion state, chloride content), corrosion current (material loss) and climatic parameters such as temperature and relative humidity were used. Such a system contains four different measuring modules (potential, current, resistance and auxiliary). These measuring modules are protected by means of a protection module against overvoltages (e.g. lightning impact). Altogether, 32 potentials, 8 currents, 24 resistances and 5 auxiliary variables can be measured. The recording interval can be flexibly selected at minute intervals. There is the possibility of connecting together up to 16 data collection systems by an RS485-network. The control and the current supply (12 V battery) of the devices take place from a central, well accessible place. The selected data are stored on the PC in a text file and can be further processed with the usual statistic software. More information about the instrumentation and the data acquisition system is given in Schiegg.[17]

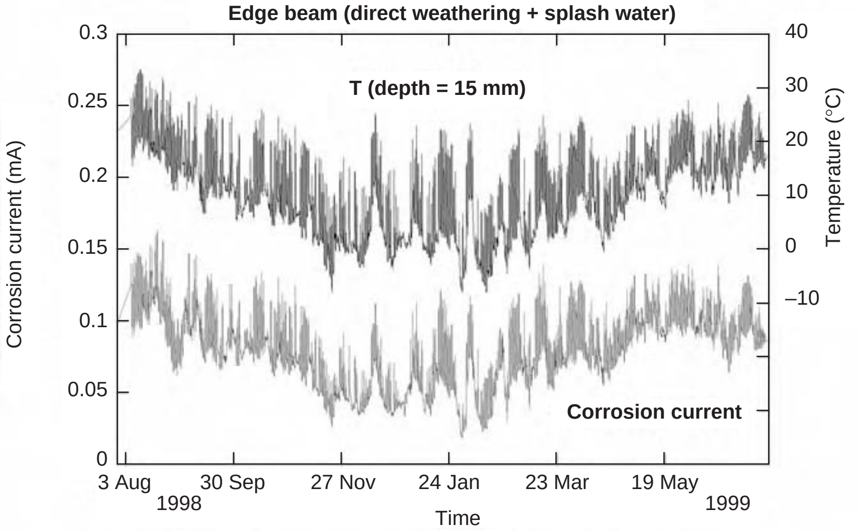
2.5.3 Results of field investigations

Reinforced concrete structures of the Swiss national highway A13 were equipped with instrumented cores and data acquisition systems for online monitoring in 1998. A number of typical exposure conditions and structures were chosen where different weathering and corrosion conditions were expected. In order to examine the influence of porosity, an instrumented core from the structure and mortar cores from the laboratory (max. grain size 4 mm, water cement ratio 0.5 and 0.6) were used.

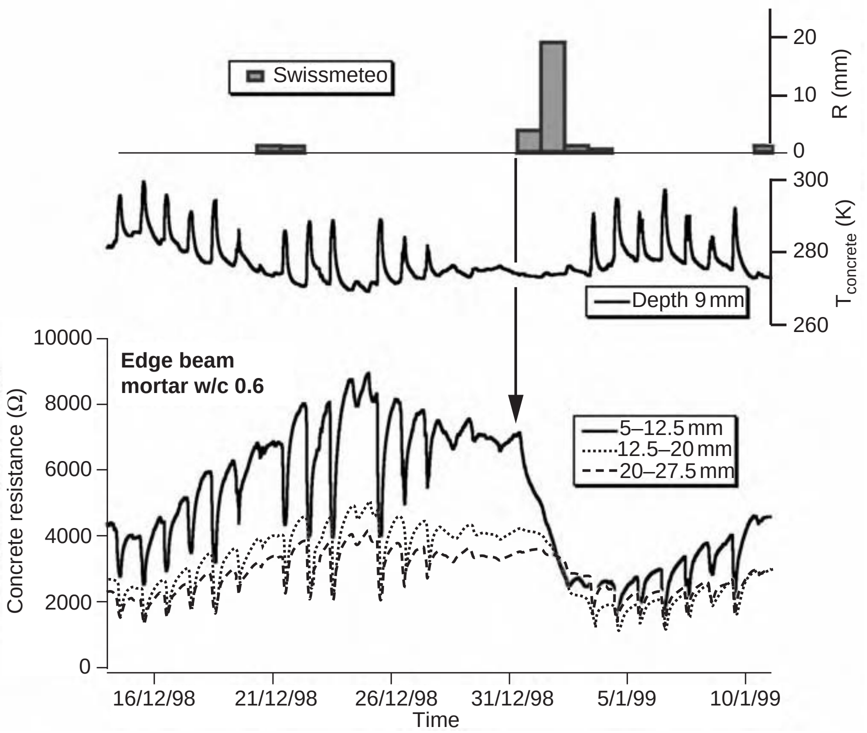
2.5.3.1 Climatic influence on concrete resistance and corrosion current

Figure 2.4 shows the corrosion current of a corroding rebar (chloride content 1.2 m%/cement) and the concrete temperature over time in the edge beam of a highway bridge during one year. There is a pronounced temperature dependence of the corrosion current (daily peaks and seasonal differences). In this example, the corrosion current differs between winter and summer by approximately a factor of 3.5 to 4. Within the daily fluctuations and the seasonal fluctuations, the increase of the corrosion current during a rise in temperature reaches a factor of 1.8 to 2.0 per 10 °C. The corrosion processes do not cease even at temperatures below 0 °C.

An important parameter influencing the corrosion rate is the concrete humidity. The concrete resistances measured by means of AC-resistance measurement provide information about humidity changes in the zone near the surface of the concrete. Figure 2.5 shows the concrete resistances over time at three depth levels in the edge beam of a highway bridge, the concrete temperature and the amount of rain for the selected time period. Similar to that shown by the corrosion current, the concrete resistance shows a pronounced temperature dependence (2.5 kΩ/10°C). After a drying period lasting until 31 December, precipitation caused a strong decrease of



2.4 Microcell current of a corroding rebar in the edge beam of a highway bridge and the concrete temperature over one year.

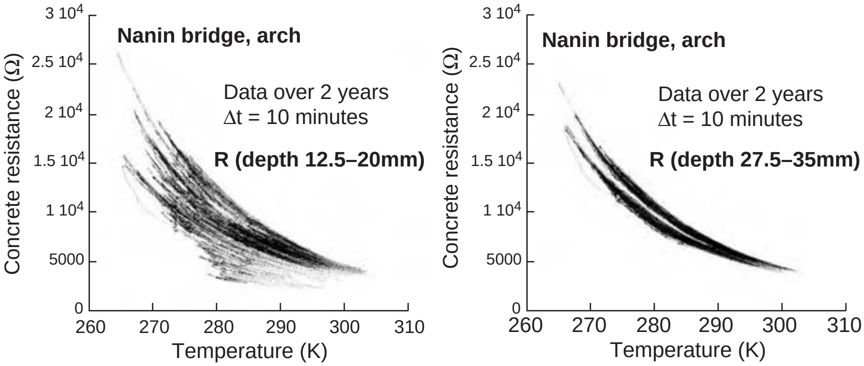


2.5 Concrete resistances over time (depth 5–35 mm) of a mortar core (w/c = 0.6) in the edge beam of a highway bridge, concrete temperature and the amount of a precipitation over time (data from Swissmeteo). December 1998 to January 1999.

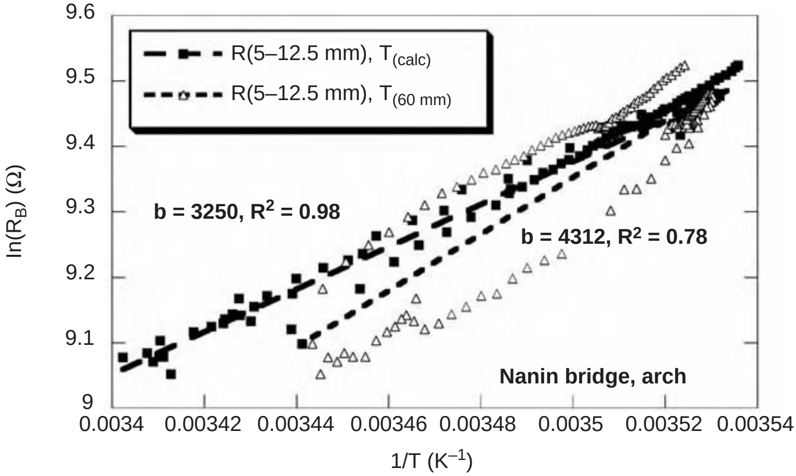
the concrete resistance in a depth of 5–12.5 mm (approx. factor 3) in the following days, whereby the gradient of the resistance decreased with increasing concrete cover. Resistance measurements show that it is possible to differentiate between wet and dry periods.

2.5.3.2 Modelling temperature dependence of concrete resistivity

For an assessment of the humidity exchange in the concrete and the consequences on the corrosion rate, changes in the concrete resistivity had to be separated from the effect of temperature. The exponential relation between the electrical concrete resistance and temperature was derived from the Arrhenius equation (Equation 2.2). In the literature, values between approximately 1500 and 5000 K for the temperature coefficients b are given[18]. In Fig. 2.6 the exponential correlation between concrete temperature and resistivity is clear. However, the variation of the concrete resistances in the depth 12.5–20 mm is much larger than in the depth



2.6 Correlation between concrete resistance and temperature for two concrete depths (12.5–20 mm and 27.5–35 mm) of a mortar core w/c = 0.5 in the arch of a highway bridge.



2.7 Determination of the b-value for two different temperatures with the ordinary least squares method. With an unfavourable temperature hysteresis loops and wrong b-values result.

27.5–35 mm. This means that the b-value is not constant but depends on concrete humidity and therefore an evaluation procedure for the exponential correlation of temperature and resistivity over time had to be developed. Since the b-value is dependent on concrete humidity, Equation 2.2 may be applied only for short time periods, during which the humidity does not change or does so only slightly. The analysis of the performed field tests, where a measuring interval of 10 minutes was selected, indicated that the determination of a b-value is optimal over 24 hours (day and night). As Fig. 2.7 shows, it is essential that measurements of the temperature and the concrete resistance are performed at the same depth from the surface in order to obtain an exact determination of the b-value. It has to be noted that the temperature gradient is not constant in a concrete structure and, because of the good heat conductivity of the concrete, gradient changes take place very quickly, but the heating and cooling rates of the concrete near the surface are different.

$$R_{T1} = R_{T0} \cdot e^{b\left(\frac{1}{T1} - \frac{1}{T0}\right)} \qquad [2.2]$$

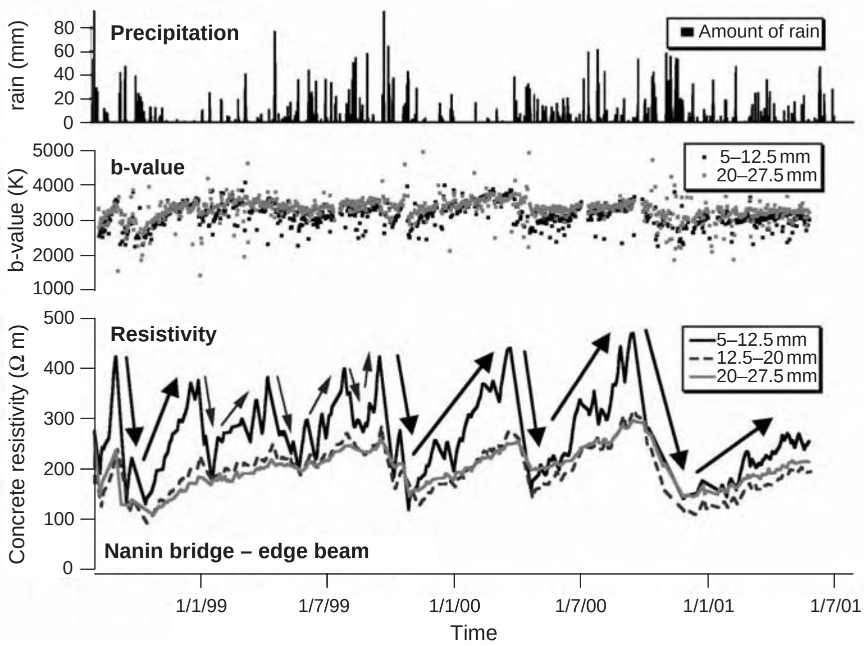
where

R_{T1} = concrete resistivity at temperature T1 [Ωm]
R_{T0} = concrete resistivity at temperature T0 [Ωm]
b = temperature coefficient [K]
T1, T0 = concrete temperature [K]

2.5.3.3 Determination of the b-values and temperature-compensation of the concrete resistance

The b-values over 24 h (144 measured values) for the temperature compensation of the concrete resistances were extrapolated with an ordinary least squares method. Figure 2.8 shows the temperature compensated (reference temperature 20°C) concrete resistivities in three depths for a mortar (w/c ratio 0.5) in the edge beam of a highway bridge, the b-values and the amount of rain. The b-values are situated between 2000 and 4000 K. The strongest fluctuations occur within the first depth level (5 to 12.5 mm), which is the result of the changing concrete humidity due to direct weathering. It is noticeable that, apart from the initial phase, strong fluctuations of the concrete humidity occur mainly in surface proximity. The transport of water and aggressive substances (e.g. chlorides) into larger depths of the concrete structure takes place about two to three times a year. This characteristic course of the concrete resistivities was found for all exposure conditions. From this behaviour short-term humidity changes which only cause a change of the humidity directly below the surface of the concrete (small incidents with transport zones <20 mm) could be distinguished from deep-reaching humidity change with transport zones over 40 mm (large incidents).

These results of the humidity transport in the concrete (wet–dry cycles) provided a new insight of the chloride transport into the concrete. The transport of chlorides into large depths of the concrete takes place during all seasons. In late autumn, winter and spring an accumulation of chlorides near the surface occurs; this is due to small incidents, i.e. chloride deposits near the surface. After drying periods large incidents of water containing

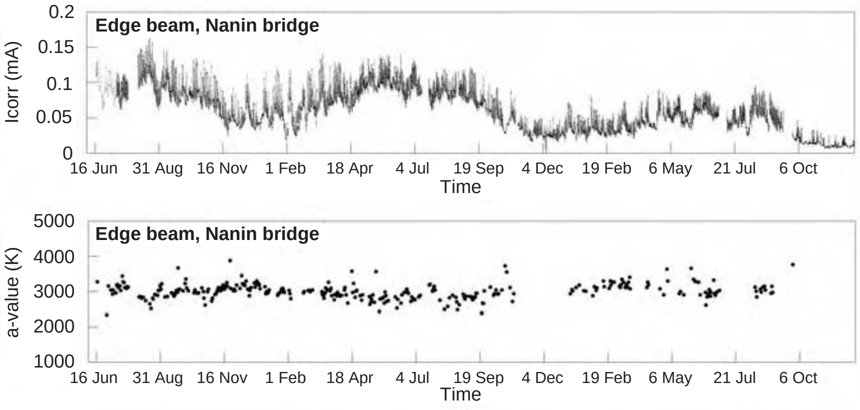


2.8 Time development of the b-values, amount of rain (data from Swissmeteo) and temperature compensated concrete resistivities of a mortar core w/c = 0.5 in the edge beam of a highway bridge (data over three years). Small/large incidents are indicated with small/large arrows.

deicing salts lead to a deep-reaching transport of chlorides. Even in summer where no chlorides are used, large incidents lead to an increase of the chloride concentration in greater depths due to the transport of water and chlorides from the outer deposits.

2.5.3.4 Temperature-dependence of the corrosion current

The modelling of the temperature-dependence of the corrosion current was performed in the same way as for the concrete resistances: The a-value in relation to the corrosion current is calculated instead of the b-value (Fig. 2.9). The comparison with Fig. 2.8 shows that a-values are situated in the same range as the b-values. With the comparison between a and b, it must be considered that the corrosion current flow takes place both over the mortar and over the concrete of the concrete structure (macrocell corrosion), while the concrete resistance is measured only within the core because of the coating on the lateral surfaces. This can entail, depending



2.9 Macrocell current over time in the edge beam of a highway bridge and related a-values, $R^2 \geq 0.975$.

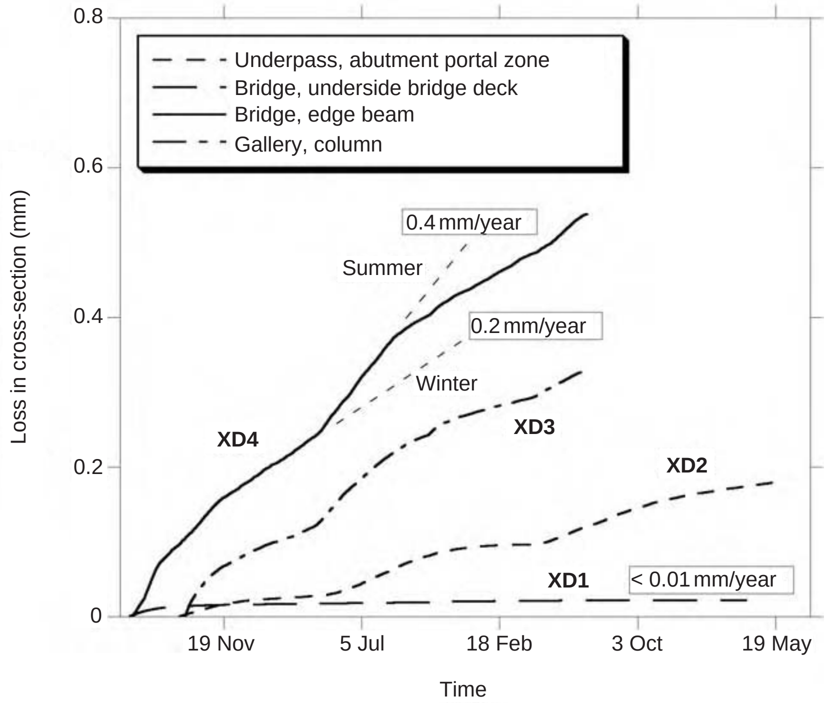
upon quality of the environment concrete, stronger fluctuations of the a-value The larger dispersion of the a-value can probably also be attributed to the fact that the corrosion current is limited not only by the concrete resistance but also by the electrochemical resistances at the anode and at the cathode. The a-values of the edge beam were about 3000 K. During laboratory tests with mortar blocks higher a-values between 4000 and 4400 K were found[19]. This suggests that the a-value, similarly to the b-value, is humidity dependent or the corrosion process in the edge beam is controlled by concrete resistivity (ohmic control). Due to the results of the field investigations no clear conclusions can be drawn as to which resistance is controlling the corrosion current which means that further investigations are necessary. A promising method is the numerical modelling of corrosion in concrete structures by means of boundary-element method analysis[20]. The results of the simulation can be used to study the influence of different parameters on the corrosion rate.

2.5.3.5 Corrosion rate and corrosion propagation

From the corrosion current measurements and the determination of active corroding areas on the rebar probes after removal of the instrumented cores the corrosion propagation (material loss over time) could be calculated using Equation 2.3:

$$G = \sum_{t} \frac{M}{Z \cdot F} \cdot I \cdot t \qquad [2.3]$$

where



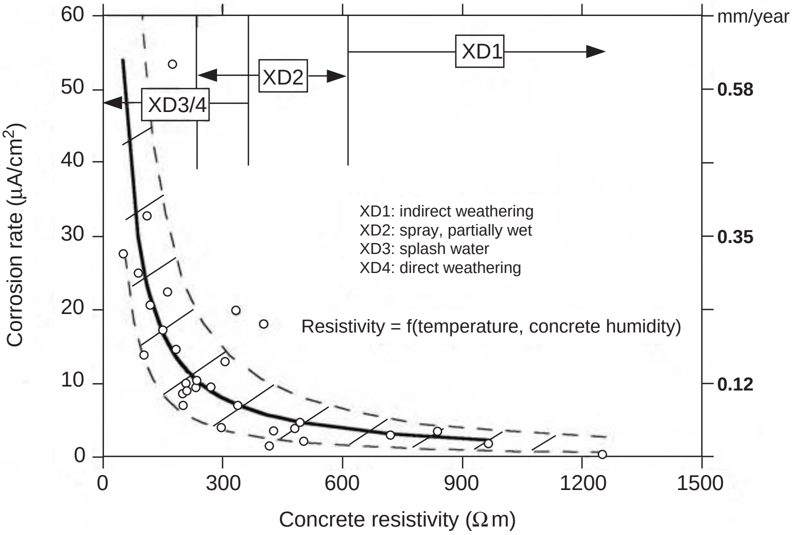
2.10 Corrosion propagation over time of corroding rebar probes in different exposed concrete structures. Exposures XD1: indirect weathering, XD2: spray, partially wet, XD3: splash water, XD4: direct weathering.

G = mass loss	[g]
M = atomic mass	[g/mol]
z = valency (Fe = 2)	[–]
I = corrosion current	[A]
t = time	[s]

Figure 2.10 shows the increase of the cross-sectional loss of differently exposed structures. Rebars in structures with direct weathering and/or splash water showed high corrosion rates up to 0.4 mm/year (0.6 mm/year in an edge beam of another bridge), whereas the propagation in partially wet structures or structures with indirect weathering was much lower (0.01 mm/year). The propagation curves showed that the decisive factor for the increase of the corrosion processes was mainly the exposure conditions of a concrete structure and, to a minor extent, the chloride content in the concrete (chloride content in each structure is higher than 1.0 m%/c). The characteristic step-shaped propagation curves had to be attributed to sea-

sonal variations of the temperature and humidity. During the summer season the corrosion rate was approximately higher than during the winter months by a factor of two. These corrosion rates agree with those obtained by practical experience.

In Switzerland 25- to 30-year-old bridges often show large areas with corrosion attacks and the high corrosion rates led to a decrease of about 10 mm of the rebar diameters. This means that in many cases the propagation period was much longer than the initiation period and the activation of the corrosion processes already started only several years after completion of the concrete construction. Regarding the prediction of the corrosion propagation a hyperbolic correlation between the concrete resistivity and the corrosion rate was found and an assignment to four different exposure conditions could be made (Fig. 2.11). This allows an estimation of the corrosion propagation rates of concrete structures to be made. There are only minor changes of the corrosion rate with concrete resistivities >300 ΩM (exposures XD2/XD1: spray, partially wet/indirect weathering). But there is a sharp increase of the corrosion rate if the concrete resistivity is <300 ΩM which is characteristic for the exposures XD3 and XD4 (structures with splash water or direct weathering). The results of the measurements showed that for the exposure conditions XD3 and XD4 corrosion rates over 20 μA/cm^2 had to be expected if concrete temperature was >10°C. For the



2.11 Correlation between concrete resistivity, corrosion rate, annual material loss and four exposure conditions for chloride-induced corrosion. Exposures XD1: indirect weathering, XD2: spray, partially wet, XD3: splash water, XD4: direct weathering.

exposure XD2 the corrosion rate was higher than 5 μA/cm^2 in the case of temperatures >10°C. These are effective temperatures and not mean values over a year which means that for the evaluation of the corrosion propagation the true temperature conditions over time have to be considered. If no temperature measurements are available data from meteo stations can be used for a primary estimation.

2.5.3.6 Conclusions

With the development and use of sensor instrumented cores as well as a data acquisition system for the continuous measuring of corrosion-relevant variables, a new measuring technique is available to monitor the corrosion of reinforced concrete constructions. The field tests at different buildings permit the following conclusions:

- The concept of monitoring the instrumented cores is well suited to practical application and provides valuable results.
- Concrete resistance and corrosion current are considerably influenced by temperature. For high quality of temperature dependence modelling of the two parameters characterisation of the temperature, by measurement or by calculation, at an exact depth from the surface is necessary.
- The temperature coefficients b (concrete resistance) and a (corrosion current) are dependent on the moisture content in the concrete and are mainly determined by the exposure conditions of the concrete structures.
- At bridge structures with direct weathering and splash water, corrosion rates up to approximately 0.4 to 0.6 mm/year are to be expected, while structures with indirect weathering clearly corrode more slowly (<0.01 mm/year). It is therefore mainly the exposure, and to a lesser extent the chloride content in the concrete, which is decisive for corrosion propagation.

2.5.4 Advantages of online-monitoring

The measurements taken over the period of two to three years showed that continuous monitoring has a decisive advantage over periodic single measurements (e.g. once a year). Some of the parameters, for instance, the resistivity and the corrosion current, are strongly influenced by the environmental conditions such as temperature and humidity and therefore important variations of these parameters can occur within one day which cannot be neglected. This means that the time at which periodic manual measurements are taken has a decisive influence on the evaluation of data and missing or incorrect consideration of the exposure conditions can lead to wrong conclusions about corrosion propagation and unsuitable repair measures. The risk of misinterpretation can be reduced by the use of short measuring intervals; short-time changes, for instance daily fluctuations, as well as long-term changes, which are due to seasonal variations, can be recorded by the new measuring technique. This procedure allows a differentiation between periods of low or enhanced corrosion activity.

2.5.5 Practical applications

By installing instrumented cores with chloride-, resistivity- and active rebar sensors in concrete structures and the use of continuous data recording the humidity transport in the surface zone of a concrete structure, the corrosion propagation can be measured. In new or repaired structures without corrosion processes it is possible to survey the chloride ingress and the corrosion initiation of the reinforcement. Furthermore, the results of the investigation show that the measurement of climatic parameters such as concrete temperature on different depths is a decisive basis for a correct evaluation and interpretation of the data. It is clear that an instrument structure with sensor devices can provide precise and detailed information about the corrosion behaviour at a particular site. Monitoring techniques that cover the entire surface of a structure (e.g. potential mapping) still have to be carried out. It is also possible to combine online-monitoring methods with manually measured instrumentation.

2.5.6 Future trends

In the future the number of reinforced concrete structures that have online monitoring devices will increase, because continuous corrosion monitoring provides an early warning system and accurately timed repair measures can lead to a significant reduction of maintenance costs. This is especially relevant for those important structures that cannot be repaired for various reasons such as costs and/or static loads. A further application is the survey of the effectiveness and durability of repair work. Online monitoring also aims at developing new repair methods, new materials or optimising repair products with the help of field investigations.

The continuous monitoring of the corrosion of steel in reinforced concrete structures has proved to be a powerful tool for the following: in determining the state of corrosion, in estimating the expected lifetime, in determining the critical period for repair, in evaluating repair efficiency and in testing the effectiveness of reconstruction measures. The currently available monitoring systems, however, require significant effort for the production of sensors, for data logger installation and for data acquisition. This results in high costs and so the use of the technique is unsuitable as a standard control method and is limited essentially to research purposes. Based on recent results in research combining an understanding of the relevant processes with the latest development in electronics it is possible to overcome many such problems. It should be possible to reduce costs of the most elaborate technology for the monitoring of reinforced concrete structures. In order to achieve this goal the following developments are required:

- Decreasing costs in production and installation: Decreasing cost for the production is achieved by industrialising the process and standardising the used components. Adapting a robust and optimised design takes the requirements of the rough environment into account. Therefore, installation of the sensor units can be carried out by construction workers on site without specific training, resulting in a significant decrease in installation costs.
- Simplification of the installation of the data logger: While the currently available systems require an understanding of the technology, the new logger design will make any wiring to the sensors obsolete. By simply plugging it to the sensor unit, the instrument will be operational. As in the simplified installation of the sensors, the setting up of the data logger does not require trained personnel, resulting in decreased costs.
- Elimination of wires for data transfer: With most monitoring systems data transfer necessitates the use of wires. This sets limits to the locations where the sensors can be installed, requires much work and cost for wiring and connection, and strongly affects the aesthetics of the construction. In order to overcome these problems each sensor unit will be equipped with a logger that communicates with a central station by wireless data transfer. A wireless communication based on GPRS will send the data from the structure to the office.

The most recent results in research demonstrated that the continuous monitoring of the state of corrosion of a construction gives much more reliable information of the actual situation. The data acquisition is automatic and continuous. Blocking of traffic, the presence of experts on site and the uncertainty of the effect of the momentary conditions during the measurement can be excluded.

2.6 Sources of further information and advice

Monitoring of corrosion is one of the principal topics in durability of reinforced concrete structures and therefore, the number of publications that refer to the survey of rebar corrosion is immense. In some newer reports further and partly more detailed information on monitoring of corrosion in reinforced concrete structures can be found[18,21,22]. Inside these reports additional references are included that give a comprehensive overview about the actual research and developments in the field of corrosion monitoring in concrete structures.

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3

Numerical modelling of reinforcement corrosion in concrete

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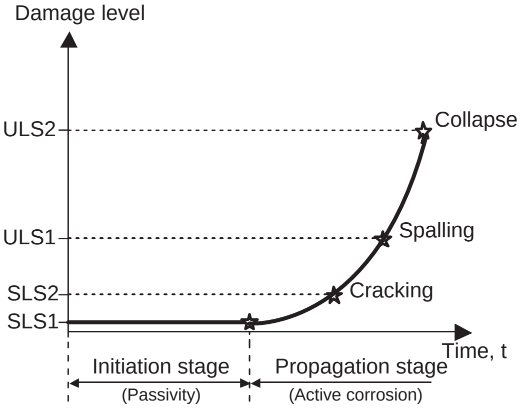
3.1 Introduction

The conventional steel grades commonly used as reinforcing steel in concrete are known to be susceptible to corrosion when directly exposed to the atmosphere. However, when embedded in cement-based concrete, steel is effectively prevented from corrosion attack due to the high alkalinity of the pore solution. This passive behaviour of steel reinforcement can be seriously compromised when the chemical composition of the pore solution is altered by carbonation or chloride contamination of the concrete cover. Most often premature corrosion of the embedded reinforcing steel results from the inappropriate use of concrete mixes, lack of quality control in mixing, and lack of sufficient concrete cover thickness[1]. The main consequences of reinforcement corrosion in concrete include a reduction in steel cross-sectional area, cracking, spalling and delamination of the concrete cover, as well as loss in bond between steel and concrete[2]. There is general agreement that corrosion of the reinforcement steel is the most prevalent form of deterioration of the infrastructure necessitating vast amounts of money for rehabilitation and repair.

In recent years a growing awareness has evolved to address explicitly durability in the design stage of new structures as well as in the management stage of existing structures. As a consequence a number of models have been developed to predict degradation over time. Most often, these models mainly focus on the initiation stage addressing the ingress of deleterious substances from the exposure environment into the concrete cover. This attention on chloride ingress and carbonation partly stems from the prevailing opinion that initiation of reinforcement corrosion defines the end of service life, despite the fact that the propagation stage may contribute significantly to service life (see Fig. 3.1).

To a considerable extent the focus on the initiation stage may also be due to the difficulties and uncertainties encountered when modelling steel corrosion in a concrete environment. However, the understanding of the basic



3.1 Simplified corrosion model for steel in concrete, comprising two subsequent stages involving initiation and propagation of reinforcement corrosion (SLS = Serviceability Limit State; ULS = Ultimate Limit State).

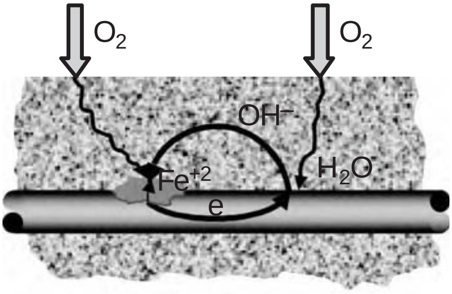
processes underlying reinforcement corrosion has improved considerably and in addition the possibilities for modelling complex electrochemical processes involved in corrosion have increased significantly during recent years. These developments will undoubtedly encourage the use of electrochemical models in favour of empirical models.

This chapter on modelling of reinforcement corrosion will only address models that predict the corrosion rate and will not discuss models involving the consequences of corrosion in terms of cracking, spalling, loss of bond, loss of cross-sectional steel area and collapse (see e.g. Al-Sulaimani et al. 1990[3], Dagher and Kulendran 1992[4], Rodríguez et al. 1996[5], Liu and Weyers 1996[6], Ohtsu and Yosimura 1997[7], Amleh and Mirza 1999[8], Hansen and Saouma 1999[9], Gulikers 2002[10]).

3.2 Electrochemical principles of corrosion

3.2.1 General

The driving force that causes metals to corrode is a natural consequence of their ability to form ions. In the aqueous medium provided by moist concrete the corrosion process is essentially electrochemical in nature comprising the transfer of electrical charge through the steel–concrete interface at anodic and cathodic reaction sites, and the simultaneous transport of ions between anodes and cathodes (see Fig. 3.2). Any metal surface on which corrosion takes place is a composite of innumerable anodes and cathodes electrically connected through the body of the metal itself.



3.2 Electrochemical corrosion process of reinforcement steel in concrete.

The predominant anodic reaction involves the oxidation of metallic iron to form dissolved ferrous ions according to:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad [3.1]$$

For atmospherically exposed concrete structures the major cathodic reaction pertains to the reduction of dissolved oxygen to produce hydroxyl ions according to:

$$O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-} \qquad [3.2]$$

The ferrous ions produced according to the electrochemical reaction shown in Equation 3.1 are subsequently changed to different forms of oxides of iron by a number of complex reactions. As both anodic and cathodic reactions involve the transfer of electrical charge it is common practice to present anodic and cathodic reaction rates in terms of electrical current densities, i_a and i_c, respectively. The anodic current density, i_a, signifies the corrosion current density, i_{corr}, which can easily be converted into a corrosion penetration rate, p_{corr}, by using Faraday's law, according to Baweja et al. 2003[11]:

$$p_{corr} = \frac{W_{Fe} \cdot i_{corr}}{z_{Fe} \cdot F \cdot G_{Fe}} \times 31.56 \cdot 10^{6} \qquad [3.3]$$

where

p_{corr} = corrosion penetration rate, [mm/year]
W_{Fe} = atomic weight for iron, $W_a \approx 56$ g/mole
i_{corr} = corrosion current density, [A/m^2]
z_{Fe} = valency of iron molecule, $z_{Fe} = 2$ [–]
F = Faraday constant, $F \approx 96\,500$ C/mole
G_{Fe} = density of iron, ≈ 7874 kg/m^3

Inserting the appropriate parameter values into Equation 3.3 implies that a corrosion current density $i_{corr} = 1\ \text{A/m}^2$ corresponds to a corrosion penetration rate $p_{corr} = 1.16\ \text{mm/year}$.

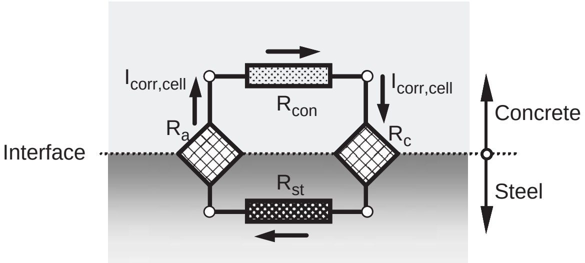
For carbonated concrete exposed to relative humidities ranging from 50 to 99 % the penetration rate may range from 1 to 50 µm/year whereas for chloride-induced corrosion the local corrosion rate may range from 9 to 122 µm/year[12]. In both situations the maximum rate is obtained at relative humidities near 95 %, but the rate drops dramatically when the relative humidity approaches 100 % due to sustained oxygen starvation. Regarding corrosion rate measurements by linear polarisation the rate of localised corrosion attack is estimated to be 4 to 8 times higher than the calculated surface averaged corrosion rate[13]. As a reference, the corrosion rate of passive steel is generally less than $1\ \text{mA/m}^2$.

An elementary electrochemical corrosion cell can be regarded as an electrical circuit characterised by a continuous flow of electrical current, see Fig. 3.3. The driving voltage, U_{cell}, equals the potential difference between anodic and cathodic reaction sites at equilibrium whereas the overall cell resistance, R_{cell}, includes contributions associated with transfer of electrical charge at anodic and cathodic sites as well as with transport between these sites. Following Ohm's law the current produced in such a corrosion circuit can be expressed by:

$$I_{corr,cell} = \frac{U_{cell}}{R_{cell}} = \frac{E_{c,o} - E_{a,o}}{R_c + R_{con} + R_a + R_{st}} \qquad [3.4]$$

where

$I_{corr,cell}$ = corrosion current produced in an elementary corrosion cell, [A]
$E_{c,o}$ = equilibrium potential of the cathodic reaction, [V]
$E_{a,o}$ = equilibrium potential of the anodic reaction, [V]
R_c = overall cathodic interfacial resistance, [Ω]
R_{con} = electrolytic concrete resistance, [Ω]



3.3 Equivalent electrical circuit for an elementary corrosion cell.

R_a = overall anodic interfacial resistance, [Ω]
R_{st} = electronic steel resistance, [Ω]

Due to the relatively high electron conductivity of steel and the usually large cross-sectional area of rebars, the contribution of R_{st} can be effectively discarded. The overall anodic and cathodic interfacial resistances also include effects of limited supply of reactants, notably oxygen diffusion to sustain the cathodic reactions. The electrolytic concrete resistance reflects the ability of cement-based concrete to convey ions through the pore system. In contrast to aqueous systems, e.g. sea water, cement-based concrete provides an electrolyte of poor ionic conductivity, characterised by resistivities ranging from 10 to 1000 Ω·m dependent on the porosity, type of cement, temperature and moisture content.

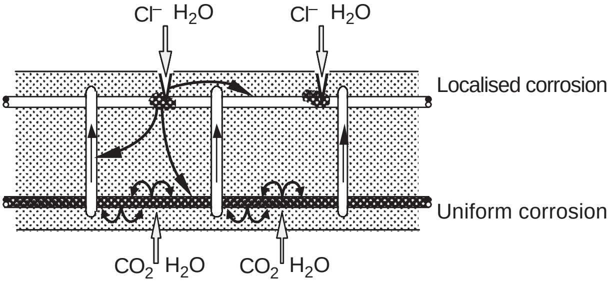
3.2.2 Micro- and macro-corrosion cells

The electrochemical nature of reinforcement corrosion allows spatial separation of anodic and cathodic sites resulting in the formation of macrocells. Localised corrosion of iron and steel, typically pitting, usually occurs by the action of macrocells. In a macrocell, the anodic and cathodic areas are macroscopic, and their locations are fixed, whereas in a microcell the anodic and cathodic sites are microscopic and their locations change randomly with time. In a macrocell relatively small fixed anodic areas surrounded by and connected to relatively large cathodic areas will suffer from accelerated corrosion attack[14].

Microcells are caused by the heterogeneity of the metal surface, such as crystal lattice imperfection, mechanical stresses and distribution of surface contaminants. Heterogeneity of the environment over the steel surface, whether due to the electrolyte phase or to the physical conditions, promotes the formation of macrocells[15]. With respect to reinforcement corrosion, macrocells resulting from differential aeration, pH and salt concentration are of practical relevance.

Normally, carbonation-induced corrosion is associated with the formation of microcells resulting in uniform corrosion attack, whereas corrosion resulting from chloride contamination stimulates the development of macrocells[16,17]. Macrocell action may also involve localised corrosion attack in the region of cracks (coplanar macrocell) and corrosion of the top layer of a bridge deck (planparallel macrocell), see Fig. 3.4.

As reinforcing steel bars are electronically connected, the complete reinforcement mesh can be regarded as an extensive electrode system with the moist concrete acting as the common electrolyte. Consequently, corrosion of reinforcing steel in concrete is influenced by the combined action of micro- and macro-cells. This electrochemical interaction will result in steel regions where either anodic or cathodic activity predominates.



3.4 Corrosion attack resulting from combined action of micro- and macro-cells.

3.3 Methods for numerical modelling

3.3.1 General

A clear distinction has to be made between empirical and electrochemical corrosion models. Whereas empirical models are based on a more general relationship between corrosion rate and some parameter that can be measured simply (concrete resistivity, relative humidity, temperature), electrochemical models are based on the electrochemical nature of corrosion.

In contrast to empirical models having the advantage of simplicity by using a limited number of parameters of practical importance, electrochemical models mostly require a considerable understanding of electrochemistry before they can be used.

3.3.2 Empirical corrosion models

3.3.2.1 Morinaga model

Based on laboratory experiments performed under well-defined conditions Morinaga[18] derived an empirical relationship between corrosion rate and a limited number of variables characterising the exposure environment. For chloride-induced corrosion the average corrosion rate is expressed by:

$$\begin{aligned} q_{corr,Cl} = {} & 2.59 - 0.05\cdot X_1 - 6.89\cdot X_2 - 22.87\cdot X_3 - 0.99\cdot X_4 + 0.14\cdot X_5 \\ & + 0.51\cdot X_6 + 0.01\cdot X_7 + 60.18\cdot X_8 + 3.36\cdot X_9 + 7.32\cdot X_{10} \end{aligned} \qquad [3.5]$$

and for carbonation-induced corrosion

$$\begin{aligned} q_{corr,CO_2} = {} & 21.84 - 1.35\cdot X_1 - 35.43\cdot X_2 - 234.76\cdot X_3 + 2.33\cdot X_4 \\ & + 4.42\cdot X_5 + 250\cdot X_8 \end{aligned} \qquad [3.6]$$

where

q_{corr} = rate of corrosion (10^{-4} g/cm^2·year)
X_1 = temperature (°C)
X_2 = corrected ambient relative humidity: $X_2 = \frac{(RH - 45)}{100}$
X_3 = relative atmospheric oxygen concentration (%/100)
X_4 = salt content (% NaCl by weight of mixing water)
X_5 = $X_1 \cdot X_2$ (interaction between X_1 and X_2)
X_6 = $X_1 \cdot X_3$ (interaction between X_1 and X_3)
X_7 = $X_1 \cdot X_4$ (interaction between X_1 and X_4)
X_8 = $X_2 \cdot X_3$ (interaction between X_2 and X_3)
X_9 = $X_2 \cdot X_4$ (interaction between X_2 and X_4)
X_{10} = $X_3 \cdot X_4$ (interaction between X_3 and X_4)

The constants have been estimated by employing multiple regression analysis. The expression is based on test results performed at temperatures of 20 and 40 °C using a salt content, oxygen concentration, and relative humidity ranging in a stepwise fashion from 0 to 3 %, 0 to 20 %, and 0 to 100 %, respectively.

3.3.2.2 Concrete resistivity model

The electrical resistivity of concrete, ρ_{con}, is considered of major importance for rebar corrosion and consequently it is one of the factors controlling the propagation stage[19]. For a given microstructure of the cement paste the concrete resistivity depends on the moisture and salt content and on the temperature[20]. Consequently, concrete resistivity indirectly reflects the prevailing exposure conditions. Alonso et al.[21] proposed an empirical model relating corrosion rate to concrete resistivity according to:

$$i_{corr} = \frac{K}{\rho_{con}} \qquad [3.7]$$

where

i_{corr} = corrosion current density, [A/m^2]
K = regression constant, K = 1 [V/m]
ρ_{con} = electrical concrete resistivity, [Ω·m]

Within the Brite EuRam II program this expression was further elaborated to include a number of correction factors[22]:

$$i_{corr} = \frac{K}{\rho_{con}(t)} \cdot F_{Cl} \cdot F_{gal} \cdot F_{Ox} \cdot F_{O_2} \qquad [3.8]$$

where

$\rho_{con}(t)$ = actual concrete resistivity at time t, [Ω·m]
F_{Cl} = factor which takes the chloride content into account, [–]

F_{gal} = factor which takes into account galvanic effects, [–]
F_{Ox} = factor which takes into account the presence of oxide layers, [–]
F_{O_2} = factor which takes into account the availability of oxygen, [–]

However, the correction factors are difficult to quantify as a substantial amount of detailed measurement data would be required[22]. As an example, the characteristic value for F_{Cl} is set at 2.63 in situations where the concrete cover is contaminated by chlorides, whereas for chloride-free concrete its value is set at 1.0.

3.3.3 Electrochemical models

3.3.3.1 General

In recent years there has been a growing tendency to develop models that address the underlying electrochemical nature of the corrosion process[23,24,25]. However, these models are often considered to be inappropriate for practical use by design and structural engineers as considerable understanding of the electrochemical principles of corrosion is required. In addition, a priori assumptions have to be made with respect to the geometrical arrangement, e.g. the location of pits and the electrochemical behaviour of the steel reinforcement, amongst others. Despite these inherent disadvantages electrochemical models may provide additional useful information on the corrosion process, in particular on the spatial distribution of corrosion attack. Moreover, these models are most suitable for the evaluation of potential mapping, cathodic protection and corrosion rate measurements.

3.3.3.2 Polarisation behaviour

Numerical modelling of reinforcement corrosion requires information on the electrochemical behaviour of the anodic and cathodic reactions involved. The electrochemistry of these reactions can be described in terms of relationships between potential and electrical current density (mostly presented on a logarithmic scale). The current density reflects the rate of the anodic or the cathodic reaction. The graphical representation of the current–potential relationship is commonly referred to as the polarisation curve. Information on the polarisation behaviour can be obtained by experimental testing of a steel electrode embedded in concrete; however, this essentially yields information on the overall polarisation behaviour of the electrode, i.e. on the combined action of the anodic and cathodic reactions. In order to allow for calculation of the spatial distribution of the rate of corrosion attack a distinction between anodic and cathodic current densities is required. This can be achieved by mathematical expressions derived from theory representing the polarisation behaviour of the anodic and cathodic reactions separately.

If the cathodic reaction is sufficiently displaced from its equilibrium potential, $E_{c,o}$, its polarisation behaviour can be expressed by the following equation[26]:

$$i_c = \frac{-i_{c,o} \cdot \exp\left(\frac{-\ln(10) \cdot (E_c - E_{c,o})}{b_c}\right)}{1 - \frac{i_{c,o}}{i_{\lim,Ox}} \cdot \exp\left(\frac{-\ln(10) \cdot (E_c - E_{c,o})}{b_c}\right)} \qquad [3.9]$$

where

i_c = cathodic current density, [A/m^2]
$i_{c,o}$ = cathodic exchange current density, [A/m^2]
$i_{\lim,Ox}$ = limiting cathodic current density, [A/m^2]
E_c = polarised cathode potential, [V]
$E_{c,o}$ = equilibrium cathode potential, [V]
b_c = Tafel slope of the cathodic polarisation curve, [V/dec]

The limiting cathodic current density takes into account the influence of oxygen diffusion through the concrete cover on the cathodic reaction. It can easily be seen that for $i_{\lim,Ox} \to -\infty$, i.e. in the absence of any diffusion control, Equation 3.9 transforms into a more familiar form:

$$i_c = -i_{c,o} \cdot \exp\left(\frac{-\ln(10) \cdot (E_c - E_{c,o})}{b_c}\right) \qquad [3.10]$$

The so-called cathodic Tafel slope, b_c, can be calculated from:

$$b_c = \frac{\ln(10) \cdot R \cdot T}{(1 - \alpha_c) \cdot z_c \cdot F} \qquad [3.11]$$

where

R = universal gas constant, $R \approx 8.314$ [J/(mol·K)]
T = absolute temperature, [K]
α_c = cathodic charge transfer coefficient, with $0.0 \le \alpha_c \le 1.0$, [–]
F = Faraday constant, $F \approx 96\,500$ [C/mole]
z_c = number of electrons involved in one reaction

For $\alpha_c = 0.67$ and $z_c = 1$ this would imply that $b_c = 176.3$ mV/dec[27].

The limiting oxygen diffusion current density can be estimated when the geometrical arrangement and the diffusional properties of the concrete cover are known. The limiting cathodic current density is attained when the maximum possible flux of oxygen from the exposed concrete surface through the concrete cover to the steel surface occurs. This extreme situation corresponds to an oxygen concentration $c_{Ox} = 0$ at the steel surface. Combined with Faraday's law the limiting cathodic current density is generally expressed by:

$$i_{lim,Ox} = -D_{Ox} \cdot \frac{c_{Ox,air}}{d} \cdot n_{Ox} \cdot F \qquad [3.12]$$

where

$i_{lim,Ox}$ = limiting cathodic current density resulting from restricted oxygen diffusion, [A/m^2]
D_{Ox} = oxygen diffusion coefficient, [m^2/s]
$c_{Ox,air}$ = oxygen concentration of concrete at the air exposed surface, [mole/m^3]
d = thickness of the concrete cover, [m]
n_{Ox} = number of electrons involved per molecule of oxygen, $n_{Ox} = 4$ [–]
F = Faraday constant, F ≈ 96 500 [C/mole]

For a cylindrical specimen containing a central steel bar $i_{lim,Ox}$ can be calculated from:

$$i_{lim,Ox} = -D_{Ox} \cdot \frac{c_{Ox,air}}{r_{st} \cdot \ln\left(\frac{r_{cyl}}{r_{st}}\right)} \cdot n_{Ox} \cdot F \qquad [3.13]$$

where

r_{st} = radius of the central steel rebar, [m]
r_{cyl} = radius of the concrete cylinder, [m]

The influence of oxygen diffusion on the rate of the cathodic reaction can also be achieved by including the oxygen concentration at the steel–concrete interface according to Kranc and Sagüés[28]:

$$i_c = -i_{c,o} \cdot \frac{c_{Ox,s}}{c_{Ox,air}} \cdot \exp\left(\frac{-\ln(10) \cdot (E_c - E_{c,o})}{b_c}\right) \qquad [3.14]$$

where

$c_{Ox,s}$ = oxygen concentration of concrete at the steel surface, [mole/m^3]

However, application of Equation 3.14 requires separate calculation of oxygen ingress through the concrete cover to the steel surface.

For the anodic reaction, in the absence of any diffusion control, the polarisation behaviour is described by:

$$i_a = i_{a,o} \cdot \exp\left(\frac{\ln(10) \cdot (E_a - E_{a,o})}{b_a}\right) \qquad [3.15]$$

where

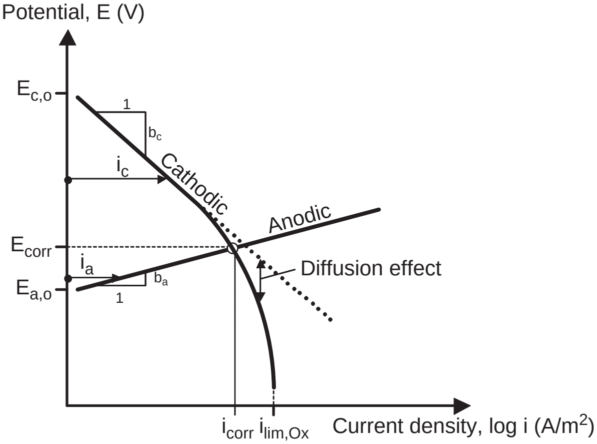
i_a = anodic current density, [A/m^2]
$i_{a,o}$ = anodic exchange current density, [A/m^2]
E_a = polarised anode potential, [V]
$E_{a,o}$ = equilibrium anode potential, [V]
b_a = Tafel slope of the anodic polarisation curve, [V/dec]

Values for the model parameters have been suggested by Kranc and Sagüés[29]: $i_{c,o} = 10 \cdot 10^{-6}$ A/m^2, $i_{a,o} = 300 \cdot 10^{-6}$ A/m^2, $E_{c,o} = -160$ mV SCE, $E_{a,o} = -780$ mV SCE, $b_c = 160$ mV/dec and $b_a = 60$ mV/dec.

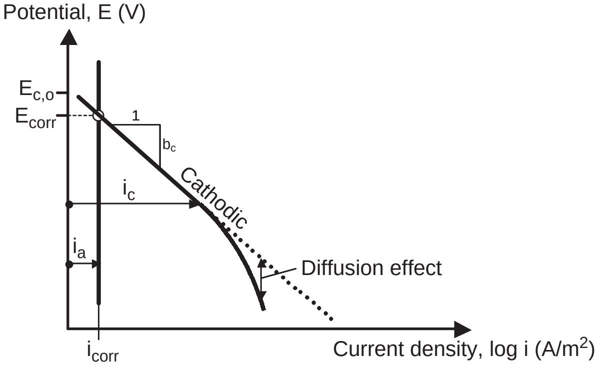
For microcell corrosion the intercept of the cathodic polarisation curve of the cathodic reaction and the anodic polarisation curve of the anodic reaction presents the situation where the anodic and cathodic reaction rates are in balance and the steel electrode adopts a common corrosion potential, E_{corr} (see Fig. 3.5). The anodic current density, i_a, at $E = E_{corr}$ is referred to as the corrosion current density, i_{corr}. For steel exhibiting ideal passive behaviour the anodic current density remains essentially constant. The resulting polarisation behaviour of the anodic and cathodic reaction is schematically presented in Fig. 3.6.

The mathematical expressions provided in Equations 3.9 and 3.15 can only be used when the equilibrium potentials of the anodic and cathodic reaction are identified as the starting point. However, values for the equilibrium potentials have to be estimated or calculated[30] in contrast to the free corrosion potential of steel reinforcement which can be measured directly using a reference electrode.

If the freely corroding condition is used as a starting point for numerical calculations, the cathodic current density of the polarised steel electrode



3.5 Schematic Evans diagram depicting the anodic and cathodic polarisation curve for actively corroding steel.



3.6 Schematic Evans diagram depicting the anodic and cathodic polarisation curve for passive steel.

can be expressed as a function of E_{corr} and i_{corr} according to Gulikers[26]:

$$i_c = \frac{-i_{corr} \cdot \exp\left(\dfrac{-\ln(10)\cdot(E - E_{corr})}{b_c}\right)}{1 + \dfrac{i_{corr}}{i_{lim,Ox}} \cdot \left[1 - \exp\left(\dfrac{-\ln(10)\cdot(E - E_{corr})}{b_c}\right)\right]} \qquad [3.16]$$

For passive steel the corrosion rate is expressed by:

$$i_{corr} = i_{pas} \qquad [3.17]$$

and the free corrosion potential by:

$$E_{corr} = E_{pas} \qquad [3.18]$$

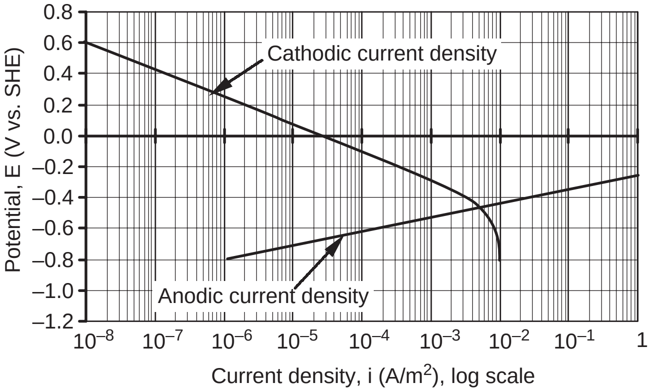
For ideal passive behaviour the anodic current density is essentially constant over a wide range of potentials and thus:

$$i_a = i_{pas} \qquad [3.19]$$

For actively corroding steel, in the absence of any limiting anodic current density, the anodic current density is again expressed by the familiar Butler–Volmer equation:

$$i_a = i_{corr} \cdot \exp\left(\frac{\ln(10)\cdot(E - E_{corr})}{b_a}\right) \qquad [3.20]$$

Values for the anodic and cathodic Tafel slope can be derived from the Stern–Geary constants B, employed for the calculation of the corrosion current density using the experimentally determined polarisation resistance, R_p. Usually, for passive steel a value of B = 52 mV and for actively corroding steel B = 26 mV is adopted[31]. Combination of these two B-values



3.7 Example of current–potential relationship for anodic and cathodic reaction with corrosion potentials used as the starting point; $E_{corr} = -0.463$ V vs. SHE, $i_{corr} = 5.184 \cdot 10^{-3}$ A/m^2, $i_{lim,Ox} = -1 \cdot 10^{-2}$ A/m^2, $b_c = 176.3$ mV/dec, $b_a = 90.7$ mV/dec.

results in $b_a = b_c = 119.7$ mV/dec. However, based on experimentally obtained cathodic polarisation curves for passive steel $b_c = 176.3$ mV/dec[32]. In order to comply with B = 26 mV this implies that for actively corroding steel $b_a = 90.7$ mV/dec.

An example of the calculated polarisation behaviour of the anodic and cathodic reaction for actively corroding steel is shown in Fig. 3.7.

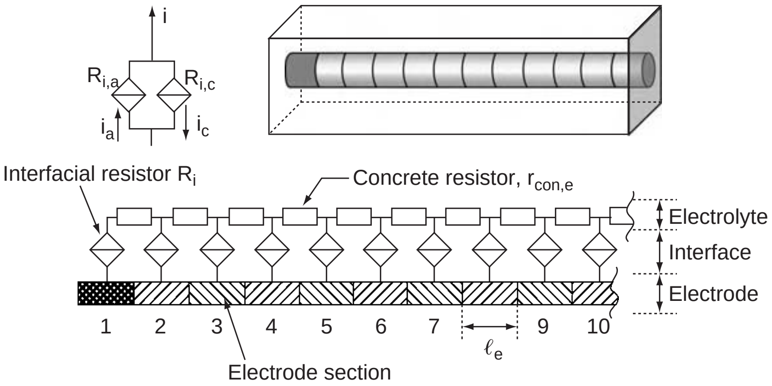
3.4 Applications of numerical models for the prediction of corrosion rates

3.4.1 General

In order to arrive at a numerical solution the corrosion problem under consideration has to be translated into a suitable geometrical arrangement. Some situations may be adequately addressed by a 1-dimensional approach, whereas other situations require a 2- or even a 3-dimensional approach.

3.4.2 Transmission line model

The so-called transmission line is a convenient way to model simple geometries of corrosion cells, e.g. so-called coplanar macrocells, using an equivalent electrical circuit following a 1-dimensional approach[27,33]. The full length of a single rebar is subdivided into a number of consecutive steel electrode sections, mostly of equal length, ℓ_e (see Fig. 3.8). The average electrochemical behaviour of each section is reflected in an interfacial resistor, R_i, made



3.8 Sectioning of a steel bar exhibiting localised corrosion attack according to a transmission line model.

up of an anodic and a cathodic component, $R_{i,a}$ and $R_{i,c}$. The magnitude of R_i is defined by the current-potential relationship described by an appropriate mathematical expression, e.g. by a combination of Equations 3.9 and 3.15, or Equations 3.16 and 3.20. The interfacial resistors R_i are placed in parallel and are interlinked by consecutive electrolyte resistors, $r_{con,e}$, placed in series. The magnitude of each electrolyte resistor is dependent on the concrete cross-sectional area, the distance between the steel sections and the concrete resistivity, ρ_{con}. For a cylindrical concrete specimen the magnitude of the electrolyte resistance is calculated according to:

$$r_{con,e} = \rho_{con} \cdot \frac{\ell_e}{\pi \cdot (r_{cyl}^2 - r_{st}^2)} \quad [3.21]$$

where

$r_{con,e}$ = element concrete resistance, [Ω]
ρ_{con} = electrical concrete resistivity, [Ω·m]
ℓ_e = element length, [m]
r_{cyl} = radius of the concrete cylinder, [m]
r_{st} = diameter of the steel bar, [m]

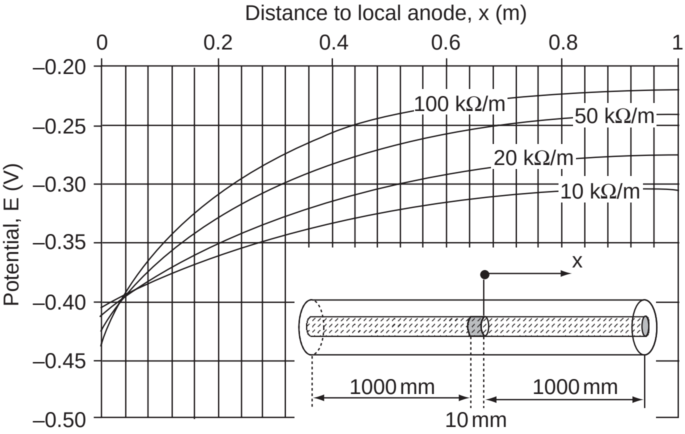
A numerical solution is achieved when the total amount of anodic current equals the total amount of cathodic current, according to:

$$\sum_{j=1}^{j=n} i_{a,j} + \sum_{j=1}^{j=n} i_{c,j} = 0 \quad [3.22]$$

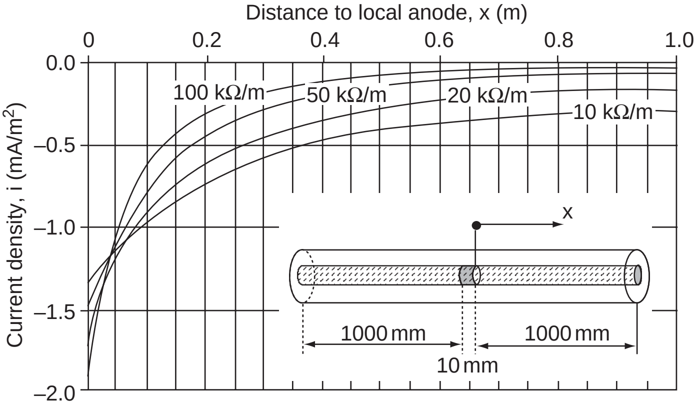
A transmission line approach is very useful to quantify the effects of crack distance on the local corrosion rate[34]. The transmission line model can easily be implemented into a spreadsheet program. The output includes the potential and current distribution. An example of the calculation results of a simple geometrical arrangement involving a small section of actively corroding steel surrounded by passive steel is provided in Figs. 3.9 and 3.10.

3.4.3 Extension to 2- and 3-dimensional models

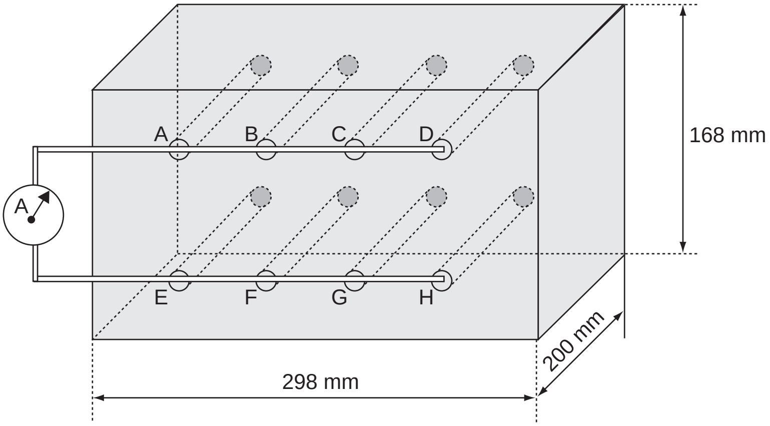
An extension to a 2- or 3-dimensional approach is required to address a number of situations occurring in practice. A 2-dimensional approach will



3.9 Potential distribution along concrete surface resulting from localised corrosion attack for a variety of lateral concrete resistances.



3.10 Current density distribution along passive steel surface resulting from localised corrosion attack for a variety of lateral concrete resistances.



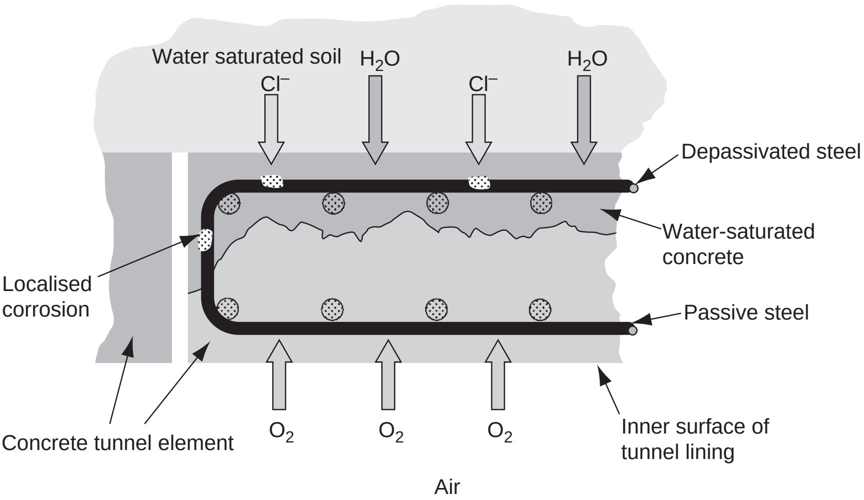
3.11 Concrete cross-section containing 8 steel electrodes addressed by a 2-dimensional resistor network[24].

be satisfactory when a concrete cross-section is considered that contains a number of reinforcement bars running in parallel with each individual bar demonstrating a uniformly distributed characteristic electrochemical behaviour over its complete circumference (planparallel macrocells). The characteristic electrochemical behaviour is expressed in terms of the free corrosion potential, E_{corr}, the steady-state corrosion current density, i_{corr}, as well as the cathodic and anodic polarisation behaviour. An example of a geometrical arrangement that can be solved by a 2-dimensional approach is shown in Fig. 3.11[24].

A 3-dimensional approach will only be justified when a number of reinforcement bars running in parallel is considered where each individual bar exhibits an essentially non-uniform electrochemical behaviour along its length, e.g. the geometrical arrangement presented in Fig. 3.4, or a complete reinforcement mesh is considered, e.g. a section of a concrete beam including main and transverse reinforcement bars as well as stirrups. In both the 2-dimensional and the 3-dimensional approach, the concrete cross-section is modelled as a network comprising discrete resistor elements[35] or a mesh of continuum resistive elements simulating the resistive properties of the concrete electrolyte. At the steel–concrete interface where anodic and cathodic currents are generated, electrical continuity has to be maintained. In order to maintain electrical charge balance the total amount of anodic current should equal the total amount of cathodic current, as:

$$\int_{A_{st}} i_a \cdot dA_{st} + \int_{A_{st}} i_c \cdot dA_{st} = 0 \qquad [3.23]$$

where



3.12 Reinforced concrete tunnel lining element exposed to different environmental conditions suffering from localised corrosion.

A_{st} = circumferential steel area, [m^2]

A convenient way to establish an electronic short circuit between the steel electrodes is achieved by connecting the steel electrodes to a common ground.

An example of a practical situation that is suitable for simulation by a 2- or 3-dimensional model is presented in Fig. 3.12. The situation concerns a concrete lining of a tunnel structure embedded in permanently water saturated and chloride-contaminated soil. The concrete elements constituting the tunnel lining contain two layers of reinforcing steel with the outer layer surrounded by water saturated concrete and locally depassivated due to the presence of penetrated chloride. In contrast, the inner layer of reinforcing steel remains essentially passive receiving adequate supply of atmospheric oxygen to sustain cathodic reactions. The potential differences generated by differential aeration and local depassivation will result in pronounced macrocell interaction which will be significantly promoted by the relatively low electrolytic resistivity of the moist concrete. This situation has been simplified in order to be modelled by a 2-dimensional resistor network[36].

3.5 Recommendations for practical use of corrosion models

Empirical models may provide a simple and practical means for the structural engineer to estimate the corrosion rate of reinforcing steel based on empirical relationships. However, these models can only be applied to general cases. Electrochemical models are most suitable to evaluate more complicated situations, e.g. macrocell interaction, localised corrosion, polarisation experiments and cathodic protection. However, these models are relatively complex requiring a considerable level of knowledge of the electrochemical principles of corrosion. Furthermore, electrochemical models require a priori assumptions on the spatial distribution of active (pitting sites) and passive steel surfaces as well as on the electrochemical characteristics in terms of free corrosion rate and free corrosion potential, i.e. prior to macrocell interaction, and anodic and cathodic polarisation behaviour. Despite these inadequacies, electrochemical models may prove to be very useful. In order to take full advantage of the possibilities of electrochemical models there is an urgent need to provide experimental data on the polarisation behaviour of actively corroding as well as passive steel.

Further information on reinforcement corrosion can be found in Schiessl[37] and in Bentur et al.[38].

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4

Influence of concrete composition

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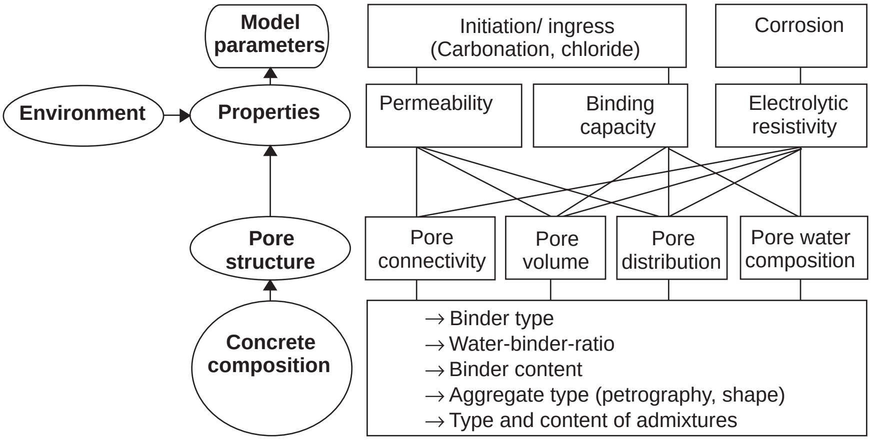
4.1 Introduction

This chapter presents the current state of the art regarding the influence of concrete composition on the overall process of reinforcement corrosion. The time dependent onset and propagation of corrosion can be described by mathematical formulae. These formulae, usually called models, reflect the reality in a more or less simplified manner. There are numerous models existing in the literature. All contain parameters that are connected by mathematical operations. These parameters define the concrete properties that dominate the ingress rate of depassivating media as well as corrosion propagation, as summarised in Fig. 4.1.

Both the concrete composition and the curing conditions determine the pore structure of the concrete. The pore structure is here described by the total pore volume, the pore size distribution, the connectivity of pores (as pores do not contribute to transport processes when blocked) and the pore water distribution.

The pore structure of the concrete when it interacts with the environmental conditions (mainly ambient humidity and temperature) determines the properties of the concrete with respect to the ingress of depassivating media (chloride, CO_2). The resistance to the ingress of media is governed by the permeability and the ability of binding penetrating substances within the pore structure. Under many practical circumstances the subsequent corrosion process is dominated by the electrolytic resistivity. These properties are usually merged into measurable input parameters for the prognosis of deterioration. The dependence of such input parameters upon the mix composition and the properties of the constituents will be discussed in the order of significance: binder type (including additions), water–binder ratio, binder content, aggregate type (mineralogy, shape), type and amount of admixtures (e.g. air entrainment agents, superplasticisers).

An essential prerequisite for any parameter within a model is that it can be measured; for any model the constituting parameters must be accessible. Measurable model parameters can be analysed to study their signifi-



4.1 Interactions between concrete composition, concrete pore structure, environmental conditions, concrete properties and resulting model parameters.

cance on the overall corrosion process. Most model parameters depend on the concrete properties listed above as well as on the relevant environmental conditions. This means that when discussing the impact of the concrete composition on reinforcement corrosion, model parameters must always be analysed in the context of environmental conditions (see Fig. 4.1). This is done in the following ways:

- In the present chapter the engineering models described were basically developed in the BriteEuram project DuraCrete, later elaborated further; they will be introduced in the coming fib-Model Code 2005.
- The techniques that measure the decisive input parameters of the models are reviewed and discussed.
- These input parameters are elaborated on with relevance both to the concrete composition and to the valid environmental conditions under which these were measured.

4.1.1 Relevant parameters for carbonation process

Some essential parameters in a carbonation model (relative humidity, curing, rain exposure) must be considered to depend both on the correlated effects of environment (e.g. effect of relative humidity and temperature are not independent) and the concrete composition. However, for the purposes of simplicity these parameters are best regarded as independent. They are determined by regression analysis regardless of the concrete composition, as the effort of testing would be excessive. The parameter that solely depends on the concrete composition is the basic carbonation resistance, and is treated in more detail in Section 4.2.

4.1.2 Relevant parameters for chloride-induced corrosion

To model the onset of chloride-induced corrosion, the depth of the convection zone Δx (Section 4.3.2), the apparent diffusion coefficient D_{app} (Section 4.3.3), the chloride concentration $C_{\Delta x}$ (Section 4.4), and the critical threshold value C_{crit} (Section 4.5) must be known. All of these parameters are influenced by the concrete composition and the environmental conditions. A discussion of the effect of the concrete composition on the ingress rate can thus only be done in the context of certain environmental exposure situations.

4.1.3 Relevant parameters for corrosion propagation phase

The model for corrosion rate as presented in DuraCrete[57] contains two main environmental and material-dependent parameters; these are the regression parameter k_0 and the electrolytic resistivity $\rho(t)$. The parameter k_0, having the units (corrosion rate × resistivity), can be obtained by performing a regression analysis of the measured corrosion current i_{corr} versus the measured electrolytic resistivity ρ in a given environment. In DuraCrete[57] Nilsson and Gehlen propose a deterministic value of $k_0 = 882$ ($\mu m\,\Omega\,m/a$) regardless of the environmental conditions and concrete composition as a temporary measure. The chloride factor F_{Cl} has been quantified without considerations of the concrete composition. The remaining factors $F_{galvanic}$ and F_{O2} are still a matter for future research. The only variable that at present seems to be sufficiently investigated is the electrolytic resistivity, which will be discussed in Section 4.6.

4.2 Carbonation resistance

4.2.1 Measurement of carbonation resistance

The carbonation resistance comprises the effective CO_2 diffusion coefficient and the binding capacity of the concrete:

$$R_{ACC,0} = \frac{a}{D_{eff,0}} \qquad [4.1]$$

where

$R_{ACC,0}$ = carbonation resistance after accelerated carbonation testing (ACC) $[(s \cdot kgCO_2)/m^5]$
a = CO_2-binding capacity of concrete $[kgCO_2/m^3]$
$D_{eff,0}$ = effective CO_2 diffusion coefficient of dry carbonated concrete $[m^2/s]$

$$a = 0.75 \cdot C \cdot c \cdot DH \cdot \frac{M_{CO_2}}{M_{CaO}} \qquad [4.2]$$

where

C = CaO content in cement [wt.-% cement]
c = cement content $[kg/m^3]$
DH = degree of hydration [–]
M = molar masses of respective substance [kg/mol]

The effective carbonation resistance of concrete can either be measured by an accelerated carbonation (ACC) test, as is done for the durability design of new structures, or by measuring the carbonation depth of an existing structure. In the latter case, the calculation model may be defined:

$$X_c = \sqrt{2 \cdot \Delta C_S \cdot R_{carb}^{-1}} \cdot \sqrt{t} \cdot W(t) \qquad [4.3]$$

where

X_c = carbonation depth [m]
ΔC_S = gradient of the CO_2-concentration $[kg\ CO_2/m^3]$
R_{carb} = carbonation resistance of concrete on site $[m^5/(s \cdot kgCO_2)]$
t = exposure duration [s]
$W(t)$ = weather function accounting for the effect of a reduction in the effective exposure time due to the water saturation of the concrete cover during and after rain [–]

and

$$R_{carb}^{-1} = k_{RH} \cdot \left(k_c \cdot k_t \cdot R_{ACC,0}^{-1} + \varepsilon_t\right) \qquad [4.4]$$

where

k_{RH} = influence of the realistic moisture history at concrete surface on D_{eff} [–]
k_c = influence of the execution (e.g. curing) on D_{eff} [–]
k_t = test-method factor [–]
ε_t = error term [–]

The carbonation resistance R_{Carb} depends on the composition, placement and curing of the concrete and, most importantly, on the ambient humidity.

The accelerated carbonation test has been chosen as a compliance test for new structures. The carbonation resistance $R_{ACC,0}$ is the result of this test and can be regarded as the potential resistance; a detailed description of the test procedure is presented in DuraCrete[1]. In summary, specimens are first produced and pre-conditioned which is essential to ensure that the drying front is ahead of the carbonation front while testing. At a defined reference age (usually 28 days) specimens are placed in a carbonation chamber with control of relative humidity (65 %) and temperature (20 °C) at a CO_2 concentration which is much higher (factor 60) than is found under natural exposure (approximately 350 ppm), but is still below those concentrations at which uncommon carbonation phases are produced[2]. After a defined test time (28 days) carbonation depth is determined at split specimens with an indicator solution (phenolphthalein). The measured carbonation depth is transferred into the carbonation resistance using the equation:

$$R_{ACC}^{-1} = \left(\frac{x_c}{\sqrt{2 \cdot \Delta C_S \cdot t}}\right)^2 = \left(\frac{x_c}{\tau}\right)^2 \qquad [4.5]$$

where

x_c = penetration depth [m]
ΔC_S = gradient of the CO_2 concentration (here 2 V.-% ≈ 0.0365 kg CO_2/m^3) [kg CO_2/m^3]
t = test duration (here t = 28 d) [s]
τ = test constant (here τ = 420) $[(kgCO_2 \cdot s/m^3)^{0.5}]$

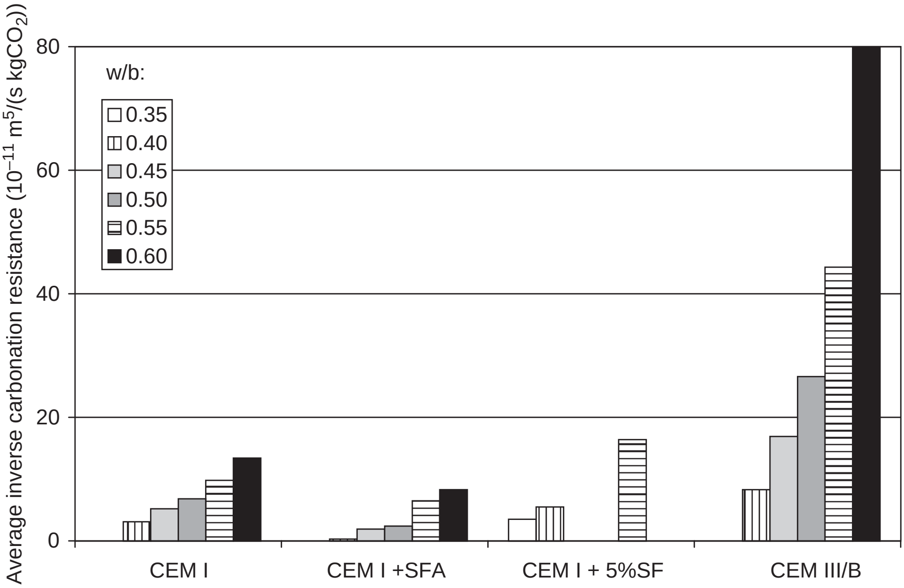
4.2.2 Influence of binder type

Concretes containing blast furnace slag show a lower carbonation resistance than do those produced from ordinary Portland cement (OPC), Fig. 4.2. When comparing the effectiveness of additions as fly ash (FA) or silica fume (SF) different relationships for carbonation resistance are obtained when compared to the standard efficiency factors $k_{addition}$ as usually applied for strength properties (compressive strength):

$$\omega_{equ} = \frac{w}{(c + k_{addition} \cdot f_{addition})} \qquad [4.6]$$

where

ω_{equ} = equivalent water–binder ratio [–]
w, c, $f_{addition}$ = mass of water, cement and additions in concrete mix [kg/m^3]
$k_{addition}$ = ratio of exchanged cement mass and necessary mass of cement addition to achieve equal properties at a defined reference age [–]



4.2 Inverse carbonation resistance $R_{ACC,0}^{-1}$ [10^{-11} m^5/(s·kgCO$_2$)] determined under accelerated conditions for various binder types and equivalent water–binder ratios ω_{equ}, according to Gehlen[3].

When applying a common equivalency factor of $k_{SFA} = 0.5$ the carbonation resistance of FA concrete is slightly higher than that of concrete with OPC. The same applies to SF concrete when using an equivalency factor of $k_{SF} = 2.0$.

4.2.3 Effect of water–binder ratio

In general, an increase in water-binder ratio (w/b) causes higher porosity and a coarser pore structure of the concrete. Higher values for w/b reduce the carbonation resistance in an exponential manner, Fig. 4.2. This effect is more pronounced for concretes that already have low potential resistance due to the binder type (e.g. slag cements).

4.2.4 Further effects of concrete composition

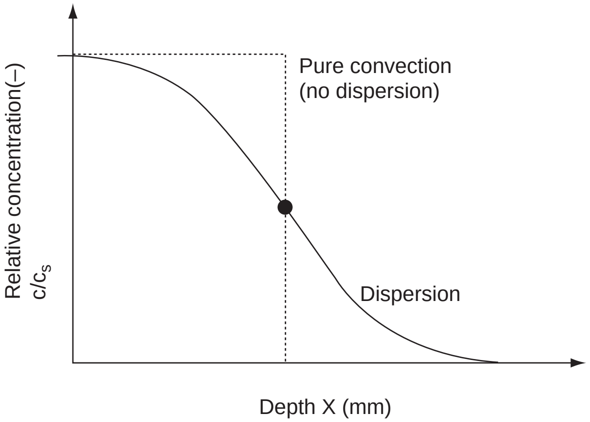
There are no systematic investigations for the carbonation resistance known to the authors regarding the effect of cement content, aggregate type or content and type of concrete admixtures. An increase in cement content increases the binding capacity which improves the carbonation resistance, as more substance for carbonation is offered. On the other hand, an increase in cement content will also increase the amount of permeable cement paste, leading to a higher effective diffusion coefficient and thus reduced carbonation resistance. These relationships are unique for each type of binder. However, within the practical domain the influence of cement content is here considered as negligible; this has already been proved for other comparable properties as chloride ingress resistance (this is discussed further in later sections). The same can be stated for the effect of aggregates and admixtures, including air entrainment.

4.3 Resistance against chloride ingress

4.3.1 Dominating transport processes

The possible processes for the ingress of chlorides have already been presented in Chapter 1. In most practical cases these are capillary suction and ingress via diffusion which is far slower. Both transport processes take place at the same time. Concrete has a very inhomogeneous pore structure, with larger pores leading to a higher velocity of the moving water meniscus in the pore. Therefore both the water and chloride fronts lag behind in small pores and are ahead in large pores, in comparison with travel in the average pore size; this is known as the dispersion effect. The consequence is that the chloride convection front does not show a sharp boundary, as would be in the case of equally sized, parallel capillaries, but is smeared along the depth as shown in Fig. 4.3.

Diffusion, i.e. the movement of chlorides within the pore water along the concentration gradient, has a similar effect as does dispersion. Both effects



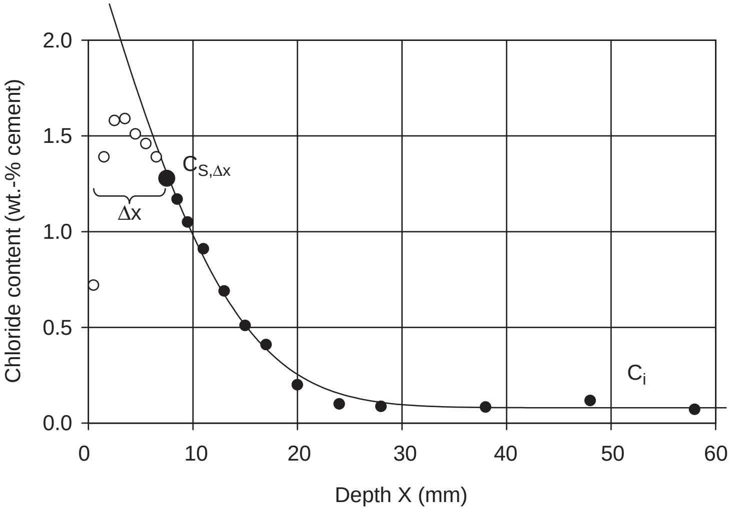
4.3 Effect of dispersion on appearance of chloride profile in concrete.

are thus modeled with a diffusion approach. Under real environmental conditions concrete is subjected to wet–dry cycles. A simple way of modeling these complicated relationships is to introduce a so called convection zone Δx. Though the main driving force is capillary suction, ingress of chlorides beyond the convection zone Δx may be modeled by a diffusion equation.

4.3.2 Depth of chloride convection zone

The convection zone (Δx) can be identified by means of chloride profiles as a maximum of the chloride concentration and is observable in the inner zone of the concrete cover, Fig. 4.4.

There are several reasons for the occurrence of a convection zone in practice: one is the leaching of chlorides in times when there is no or low chloride loading which only occurs if the concrete surface is subjected to chloride-free water. Moreover, chlorides are carried along with the chloride-free water entering the concrete. Due to the effect of dispersion the concentration profile results in an increasingly elongated shape. During ingress of chloride-free water, already inherent chlorides are dragged in, thus resulting in a maximum peak. Moreover, carbonation of the concrete during drying phases will reduce the binding capacity whereby bound chlorides are set free in the zone near the surface. This enhances the chloride gradient. Chlorides that have been set free at the near surface zone are thus

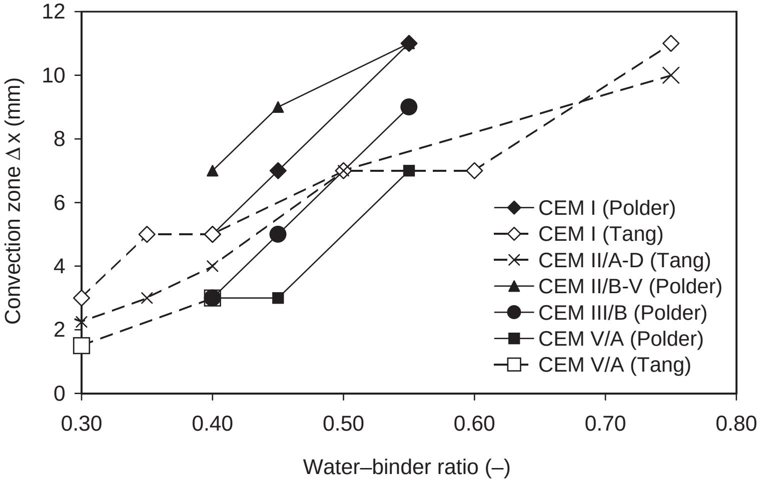


4.4 Typical chloride profile from splash zone in road environment. Profile has been fitted to 'error function solution' neglecting data points in convection zone Δx.

forced into the inner domain where the binding capacity is still larger and so the maximum peak is even enhanced.

In marine structures leaching of chlorides can take place in the atmospheric zone. For structures in the road environment chlorides are washed out and dragged in close to the road edge by splash and spray water of the traffic or by rain if the structure is not sheltered. The occurrence of a convection zone is therefore dependent on the position of the surface with respect to the source of chloride-free water. Gehlen[3] analysed 127 chloride profiles in the marine environment without distinguishing either the distance to chloride source nor the concrete composition and obtained an average depth of $\Delta x = 8.9$ mm. Schiessl and Lay[10] analysed the convection zone for mainly sheltered concrete surfaces in the road environment. If a surface is situated within the domain of 3 m above the road level and 2 m from the road edge (spray zone), a convection zone will be likely to occur. In the splash zone an average of $\Delta x = 9.0$ mm was obtained (existing structures are mostly produced with OPC; w/b-ratios are assumed to be in the domain of 0.4–0.55).

Systematic data with respect to the influence of concrete composition on the depth of the convection zone is scarce. Very precise chloride profiles (grinding depth intervals of 1 mm) from the literature with peaks as shown in Fig. 4.4 were analysed with respect to effects upon the convection zone Δx, Fig. 4.5. From Fig. 4.5 it can be concluded that a rise by 1/10 in w/b-ratio



4.5 Effect of binder type and water–binder ratio on depth of convection zone Δx. Chloride profiles from exposure tests (field station Träslövsläge, Sweden) in atmospheric and tidal marine zone[4] and wet–dry cycles in laboratory tests performed by (Polder and Peelen)[5] (26 cycles; 1 day in 3 %NaCl; 6 days dry at 20 °C/50 %RH; each data point reflects the average of 6 chloride profiles).

will lead to an increase of the convection zone of around 2 mm. Even at w/b ratios as low as w/b = 0.30 a convection zone of 2–3 mm must be expected. The use of additions or blending agents such as silica fume, fly ash or blast furnace slag (CEM III/A or B) will reduce the depth of the convection zone by up to around 60 % compared with that of ordinary Portland cement (CEM I).

4.3.3 Types of chloride diffusion coefficients

In the current literature there is a great deal of disagreement regarding the terminology for diffusion coefficients. There are real (D), effective (D_{eff}), apparent or achieved (D_{app} or D_a), steady state (D_{ss}), non-steady state (D_{nss}), potential (D_p), and other diffusion coefficients. A consistent definition of these terms is currently aimed for but not yet achieved in the RILEM-TC-178. In order to avoid confusing the reader, the terminology as used in this manual is described here briefly.

4.3.3.1 Effective chloride diffusion coefficient D_{eff}

The effective diffusion coefficient D_{eff} is the result of diffusion cell tests. In these a thin concrete specimen separates a chloride-free and a chloride-containing solution. Firstly the chloride concentration of the chloride-free solution is measured vs. time. Once a steady ingress rate is reached, D_{eff} is calculated according to Fick's first law. D_{eff} can also be determined by accelerated tests as for instance standardised in NT BUILD 355, 1997[6]. The effective chloride diffusion coefficient D_{eff}:

(a) Is considered to be a pure material specific parameter.
(b) Is a measure of the permeability (porosity, pore distribution and pore connectivity) of the concrete with respect to chlorides at the age of testing under water-saturated conditions.
(c) Does not include binding processes and is thus a steady-state diffusion coefficient.
(d) Includes the different transport velocity of anions and cations.
(e) Will decrease with age due to hydration (testing must therefore take place at different ages to obtain an age-dependent function).
(f) Increases with rising temperature in an exponential manner (testing must therefore be conducted at the same age at different temperatures).

For prediction purposes D_{eff} as such is of little use, because the following effects are not incorporated:

(g) Chloride binding reduces the ingress rate. Chloride binding is a time-dependent process, which takes place in a non-linear fashion in dependence on the chloride concentration, (see Chapter 1). As the chloride concentration at a certain depth in the concrete changes constantly with time, the diffusion coefficient will change with time as well.

(h) The ingress rate and thus the diffusion coefficient drops by several orders of magnitude for lower degrees of water saturation of concrete (see Chapter 1). The degree of water saturation and thus the diffusion coefficient in the concrete cover will in most practical cases change with time.

(i) A pure diffusion approach assumes that there are no interactions between the moving substances but in reality the charges of ions interact. Chlorides move faster than the accompanying cations and will thus be slowed down by their presence. Moreover, a rise in concentration will also reduce the velocity of chlorides, due to reduction of chemical activity and interactions with similarly charged ions at the pore walls.

4.3.3.2 Apparent diffusion coefficient D_{app}

The above mentioned aspects (a) to (i) demonstrate the complexity of chloride ingress into concrete. Nevertheless, all of these aspects must be considered to establish a function for a diffusion coefficient which enables a realistic prediction under real environmental conditions. The average value during a certain exposure time of the so called apparent diffusion coefficient D_{app} is obtained in combination with the chloride concentration in the surface layer of the concrete in the given environment, by fitting the error function solution of Fick's second law of diffusion to chloride profiles obtained under real environmental conditions during structure investigations, see e.g. (LIFECON[11]), NT BUILD 443[7] and Fig. 4.4. The aspect (g) can be taken into account by:

- Determining chloride binding isotherms in dependence of concrete composition, which are used in combination with D_{eff}. A binding isotherm is the relationship between chloride concentration in exposure solution, C_{free}, and the bound chloride content, C_{bound}, being the difference of the total (measurable) and the free chloride content (see Chapter 1).

$$D_{app} = \frac{D_{eff}}{p \cdot \left(1 + \frac{\partial c_{bound}}{\partial c_{free}}\right)} \qquad [4.7]$$

where

D_{app} = 'apparent' diffusion coefficient (non-steady state diffusion) [m^2/s] (including binding of chlorides)

D_{eff} = effective diffusion coefficient (steady state diffusion) [m^2/s]
p = porosity of concrete [–]
$\frac{\partial c_b}{\partial c_f}$ = chloride binding capacity, being the ratio of bound and free chlorides [–]

- using finite difference methods to incorporate the depth dependence (numerical modelling).

The aspect (h) can be included by performing diffusion tests in a non-saturated state. The common diffusion cell is thus not applicable any longer as concrete in this test set-up is always in a saturated state. In a few research works, e.g. Climent[8], a finite quantity of chlorides was applied at the concrete surface and specimens were kept at preset water saturation degrees. After a certain time specimens were used to determine chloride profiles. A mathematical solution of Fick's second law which is valid for a changing surface concentration must be fitted to the profiles to obtain the diffusion coefficient. Moreover, the time-dependent chloride binding process as described in (g) must be considered in the evaluation.

The aspects (g) and (i) can be incorporated indirectly into the diffusion coefficient by applying a time-dependent reduction (age) factor. The apparent diffusion coefficient D_{app}:

- Is thus not a material parameter, but must be considered as a regression coefficient (D_{app} and $C_{\Delta x}$ are not independent) which quantifies the permeability of a specific concrete under specific environmental conditions.
- Does include all of the mentioned environmental effects, but the separate contributions of these effects is not known from a single chloride profile.
- Is only an average value for the regarded exposure time, but will change with time (various chloride profiles at different ages are required to establish a time-dependent relationship).

The apparent diffusion coefficient D_{app} depends on basic material properties, which in turn depend on the concrete composition, execution parameters (e.g. curing) and environmental conditions (water saturation, temperature, see Fig. 4.1), and can be described as follows[9]:

$$D_{app}(t) = \frac{\int_{t_0}^{t} D_{RCM,0}(t) \cdot k_T \cdot k_w \cdot \left(\frac{t_0}{t}\right)^{n_1} dt}{(t - t_0)} \qquad [4.8]$$

where

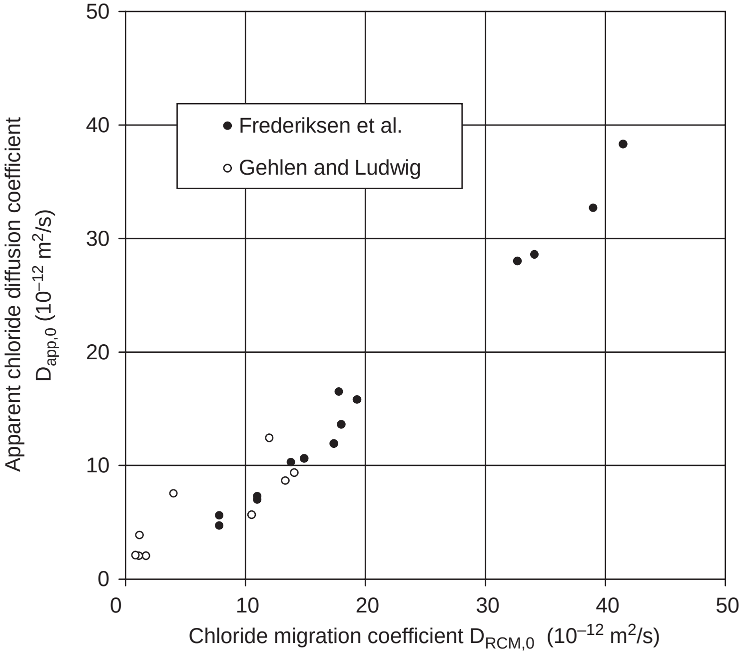
$D_{app}(t)$ = time-dependent apparent diffusion coefficient of concrete [m^2/s]
$D_{RCM,0}$ = time-dependent chloride migration coefficient of water-saturated concrete prepared and stored under predefined conditions, [m^2/s]
n_1 = exponent regarding the time dependence of D_{app} due to the environmental exposure [–]
k_T = temperature parameter [–]
k_w = factor to account for the degree of water saturation w of concrete [–]
t = age of concrete [s]
t_0 = reference time [s]

All of the above given parameters must be considered as dependent on both composition and age of concrete. Complete quantification has currently only been achieved for the chloride migration coefficient $D_{RCM,0}$ for a broad variety of concrete compositions. The environmental transfer factors are obtained by collecting chloride profiles from structures or specimens produced with different concrete types under various exposure conditions. For these a regression analysis can be performed to separate the different effects on D_{app}[3,10].

The chloride diffusion coefficient is highly dependent on the concrete composition. The experimental determination of chloride diffusion coefficients of concrete by conventional methods (involving diffusion-cell tests or immersion tests), are very time consuming. In immersion tests concrete samples are kept submerged in a chloride-containing solution to measure the chloride ingress after certain testing periods by withdrawal and chemical analysis of dust samples, thereby obtaining chloride ingress profiles. An apparent diffusion coefficient can be derived by making use of curve-fitting methods based on Fick's second law of diffusion on the obtained chloride profiles. In turn the so called rapid chloride migration coefficient $D_{RCM,0}$, determined in an electrically accelerated test, offers the following benefits:

- For equal concrete compositions the chloride migration coefficient $D_{RCM,0}$ shows a strong statistical correlation with effective diffusion coefficients D_{eff} (determined by time-consuming immersion tests) (see Fig. 4.6).
- A short test duration is achievable with the RCM test.
- The RCM test is a robust and precise method.

Thus $D_{RCM,0}$ serves well to quantify the effect of the basic influences resulting from the concrete composition and it has been used thus in the following sections.



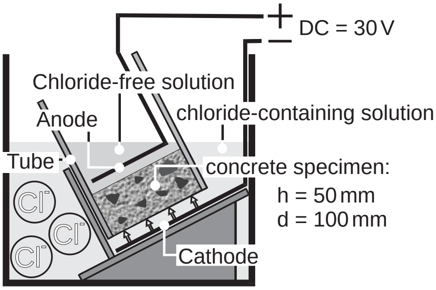
4.6 Correlation of the apparent diffusion coefficient obtained by immersion tests and the chloride migration coefficient $D_{RCM,0}$ (Gehlen[3]; Frederiksen et al.[29]).

4.3.4 Measurement of rapid chloride migration coefficient $D_{RCM,0}(t)$

The principle of the test method is the acceleration of ions by means of an electrical voltage gradient, Fig. 4.7. Details on the electrically accelerated RCM test method and further investigation methods concerning the effective diffusion coefficient are provided in LIFECON[3,10]. The 90 % quantile of deviations from the mean value of repeated measurements (equality of concrete composition, laboratory and personal: reproducibility) of the migration test is around 20 %. This can be taken as a measure of whether an influence is to be regarded as significant or not.

4.3.5 Effect of binder type on chloride diffusion coefficient

Binder types can be categorised according to the content of amorphous (reactive) calcium oxide (CaO). One can distinguish hydraulic binders (ordinary Portland cement) with around 65 % CaO, latent hydraulic (blast



4.7 Experimental design of the rapid chloride migrations test (RCM).

Table 4.1 $D_{RCM}[10^{-12} m^2/s]$ of concrete produced with OPC (CEM I) at an age of 28 d, according to Gehlen[3], DuraCrete[13], Schiessl and Wiens[14] and Lay et al.[22]

Reference	w/b				
	0.40	0.45	0.50	0.55	0.60
Gehlen	8.9	10.0	15.8	19.7	25.0
DuraCrete	8.1	–	13.2–16.1	–	23.3
Schiessl and Wiens†	8.7	–	12.4–12.9	–	29.1
Lay	5.0	5.7–18.6††	9.3	11.1	13.5

† tested on mortars.
†† to demonstrate the variation, binders of different plants were tested.

furnace slag) with around 45 % CaO, pozzolanic (fly ash and silica fume) with around 10–15 % CaO and inert (e.g. additions of limestone) with around 0 % reactive CaO. The effect of the binder type upon the diffusion coefficient will be discussed according to the reactivity.

4.3.5.1 Ordinary Portland cement (OPC)

Portland cement (CEM I) contains around 65 % of the CaO rich calcium silicate phases (C_2S and C_3S), which react with the mixing water and are mainly responsible for the mechanical properties of hardened concrete.[12] Table 4.1 provides an overview of the range of values to be expected. The diffusion coefficient decreases with increasing hydration, which in turn increases with the age of the concrete, with increasing temperature and fineness of the cement.

4.3.5.2 Slag

Ground granulated blast-furnace slag (GGBFS) is a byproduct of steel production, which is formed when molten iron blast-furnace slag is rapidly cooled in water. GGBFS behaves as a latent hydraulic material. The CaO content is lower compared with that of OPC. The latent hydraulic reaction requires calcium hydroxide $Ca(OH)_2$ provided by the OPC and is much slower than the hydration of OPC and so the effect of the concrete age is even more pronounced. The portion of capillary pores is reduced significantly with age, as the pore size distribution is shifted to a finer domain when compared with Portland cement. As more gel pores are produced physical chloride binding is enhanced. These aspects explain the reduction of the apparent diffusion coefficient with time as has been frequently observed[15,16,17]. An overview of test results from literature data is provided in Table 4.2.

4.3.5.3 Effect of fly ash

Fly ashes (siliceous or calcitic) are fine residues of the combustion of ground or powdered coal. They are usually in the range of fineness of cement and consist mainly of more or less spherical, glassy particles as well as residues of hematite, magnetite, char and some crystalline phases formed during cooling. Amorphous silicates (SiO_2) and aluminates (Al_2O_3) of the fly ash react in an alkali rich environment to CSH phases. As the pozzolanic reaction of the fly ash takes place very slowly, the portion of capillary pores is reduced with proceeding hydration. A major contribution of the fly ash

Table 4.2 $D_{RCM}[10^{-12} m^2/s]$ of concrete produced with blast furnace slag at an age of 28 d[3,13,14,22]

Binder	Reference	w/b				
		0.40	0.45	0.50	0.55	0.60
CEM II/B-S	Gehlen	4.2	–	–	–	–
	Lay	4.9	6.9–7.7[††]	8.3	–	–
CEM III/A	Gehlen	2.4–2.5	–	–	–	–
	Schiessl and Wiens	–	–	4.8	–	–
	Lay	4.0	3.9	4.2	–	–
CEM III/B	Gehlen	1.4	1.9	2.8	3.0	3.4
	DuraCrete	–	–	1.3–2.7	–	–
	Schiessl and Wiens[†]	–	–	2.3	–	–
	Lay	2.3	1.7	1.8	–	–

[†] tested on mortars.
[††] to demonstrate the variation, binders of different plants were tested.

is the possible complete blocking of the capillary pores by hydration products, which then do not contribute to the transportation processes, as shown in Table 4.3.

4.3.5.4 Effect of silica fume

Silica fume is a by-product of the reduction of high purity quartz with coal in electric furnaces during the production of silicon and ferrosilicon alloys. Silica fume consists of very fine glassy spherical particles with a high content of amorphous SiO_2. The average grain size is around 100 times smaller than that of cement[12]. Silica fume additions lead to a very fine pore structure. Nevertheless, it is a well-known fact that addition of silica fume must be limited because these consume hydroxides during hydration; addition of 15 to 20 % can result in a total consumption of the $Ca(OH)_2$ content and the pH may fall close to 12.5 by 28 days. With content of up to 10 % the corrosion protection appears to be unaffected. The effect of the silica content upon the chloride migration coefficient can be seen from Table 4.4.

Table 4.3 $D_{RCM}[10^{-12}\,m^2/s]$ of concrete produced with fly ash (FA) at an age of 28 d[3,14,22]

Binder	Reference	w/b				
		0.40	0.45	0.50	0.55	0.60
CEM I + 15 %FA	Gehlen	5.6	6.9	9.0	10.9	14.9
	Lay	–	5.1–12.3†	–	–	–
CEM I + 20 %FA††	Schiessl and Wiens	6.1	–	14.0	–	22.3
CEM I + 40 %FA	Schiessl and Wiens	–	–	9.7	–	–
CEM I + 60 %FA	Schiessl and Wiens	–	–	8.3	–	–

† to demonstrate the variation, binders of different plants were tested.
†† coarse fly ash.

Table 4.4 $D_{RCM}[10^{-12}\,m^2/s]$ of concrete produced with silica fume (SF)[3,18]

Binder	Reference	w/b						
		0.30	0.35	0.40	0.45	0.50	0.55	0.75
CEM I + 5 %SF†	Gehlen	–	4.4	4.8	–	–	5.3	
CEM I + 5 % SF††	Lindvall	0.6	1.6–4.4	2.7–5.3		13.4		33.9
CEM I + 10 % SF††		0.3		3.2				

† tested at 28 days.
†† tested at 180 days.

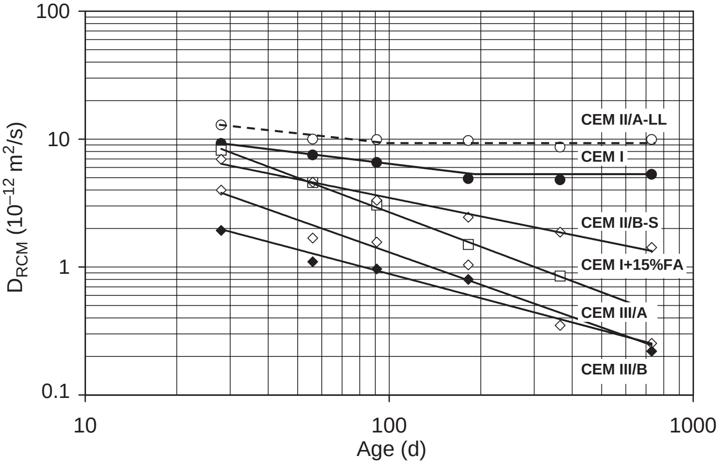
4.3.5.5 Effect of limestone

Limestone has no pozzolanic abilities and thus does not contribute to the development of CSH-phases; it acts mainly as a filler through the portion of Portland cement in the binder. Moreover, limestone in exchange for a certain portion of OPC in the binder becomes increasingly important through the reduction of emissions of CO_2 per mass unit during production. Ponding experiments in Bonnavetti et al.[19] indicate that the chloride penetration depth is increased by around 40 to 115 % when using 10 to 20 % limestone in exchange for Portland cement. Investigations by Lay et al.[22] also showed an increase in rapid chloride migration coefficient by around 30 % when using around 15 % limestone in the cement. The resistance towards chloride ingress is hence reduced.

4.3.5.6 Summary on the effect of binder on chloride diffusion coefficient

Investigations by Lay et al.[22] revealed that the most useful classification is that according to the type of binder, whereas data with different cement strength classes and cement factories (large scatter between factories) should be merged, as was done to obtain the relationships given in Fig. 4.8.

From Fig. 4.8 it can be derived that the application of additions such as fly ash (CEM I + 15%FA) and blast furnace slag (CEM II/B-S, III/A and III/B) considerably reduce the migration (diffusion) coefficient when compared with ordinary Portland cement (CEM I) or Portland cement with



4.8 Mean values for rapid chloride migration coefficient D_{RCM} vs. age in days for various binder types according to EN 197 from different German production sites (all concretes with w/b = 0.45)[10].

additions of limestone (CEM II/A-LL). This effect becomes even more pronounced at a higher concrete age.

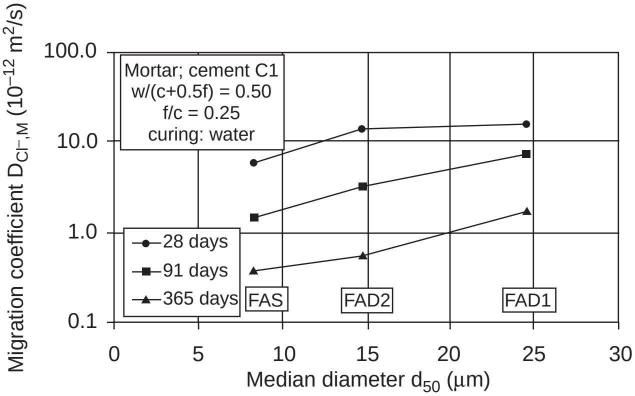
4.3.6 Effect of binder fineness on chloride diffusion coefficient

Hansson and Sørensen[20] tested sulfate-resistant Portland cement with different degrees of fineness. Diffusion cell tests were conducted at an age of 28 days. A clear trend regarding the influence of the cement fineness could not be observed. However, Schiessl and Wiens[14] found a significant influence of fly ash fineness upon the migration coefficient. With increasing average particle diameter d_{50} an increase in migration coefficient was observed, Fig. 4.9.

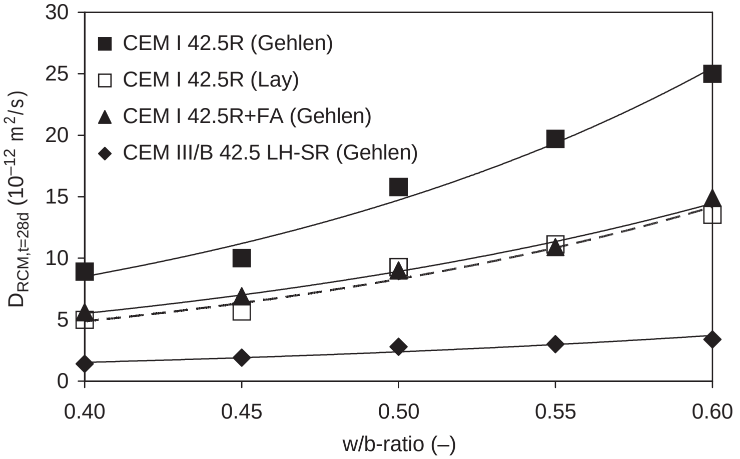
4.3.7 Effect of water–binder ratio on the chloride diffusion coefficient

Following the results of Frederiksen and Geiker[21] from exposure tests in sea water an exponential approach seems to be the most suitable in describing the effect of the w/b-ratio.

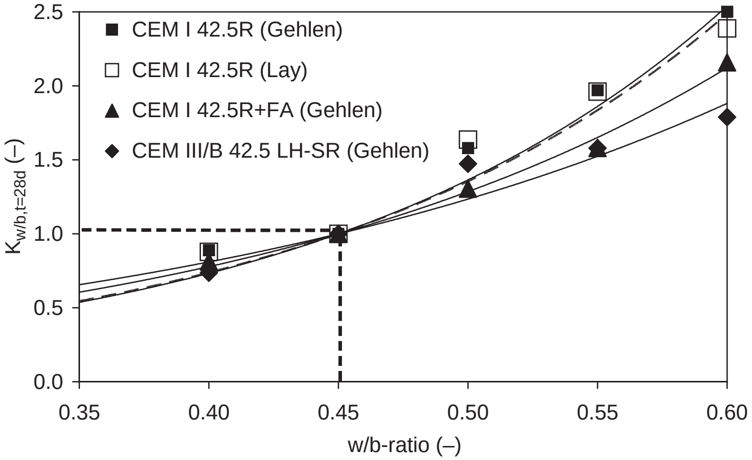
Results are shown in Figs 4.10 and 4.11. In the practically relevant domain the effect of the w/b-ratio can be regarded as independent of the concrete age. This is exemplified in Fig. 4.12, as the curves for various w/b-ratios can be shifted along the ordinate.



4.9 Effect of fly ash fineness on chloride migration coefficient[14].



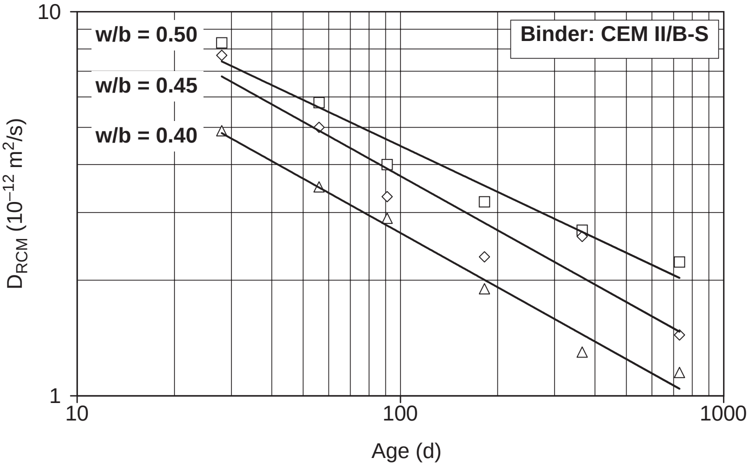
4.10 $D_{RCM,\,t\,=\,28\,d}$ versus w/b-ratio for different binder types using data from Gehlen[3] and Lay et al.[22]



4.11 Binder specific factor $k_{w/b,t\,=\,28d}$ to account for changes in w/b-ratio calculated by relating original data given in Fig. 4.10 to the value measured at w/b = 0.45.

4.3.8 Effect of cement content on the chloride diffusion coefficient

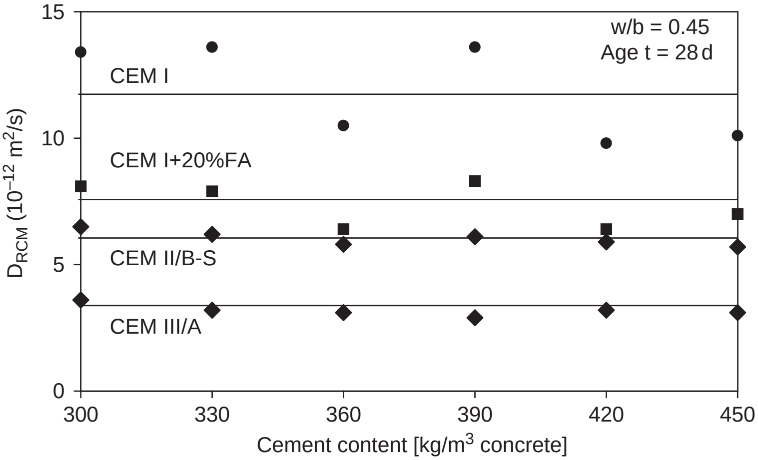
Impermeable aggregates can be regarded as obstacles within concrete, increasing the length of the transport paths; this effect can be described using the technical term ‘tortuosity’. Higher cement contents increase the volume of porous cement paste at constant water-binder ratio and a reduc-



4.12 Chloride migration coefficients D_{RCM} vs. age in days for concrete produced with 360 kg/m^3 CEM II/B-S 32.5 at w/b-ratios from 0.40 to 0.50.

tion of cement paste volume would therefore reduce the diffusion coefficient. However, a certain minimum cement paste volume is required to fill the space within the aggregates and to ensure sufficient workability of fresh concrete.

If the cement content is changed for a constant w/b-ratio, various aspects with opposing effects have to be considered. These can be positive (+) or negative (–) with respect to the resistance towards chloride ingress. It is generally accepted that the interfacial zone around the aggregates is more porous than the bulk cement paste matrix (–). If the cement paste volume increases the relative portion of the interfacial zone is reduced (+) as is the tortuosity at the same time (–), whereas the portion of the bulk volume increases (–). These complicated relationships are best analysed experimentally. Buenfeld and Okundi[28] determined the apparent diffusion coefficient by fitting chloride profiles to the error function solution (see Section 4.4.3), subsequent to ponding tests. They found a slight steady increase in diffusion coefficient with rising cement content in the domain of 300 to 450 kg cement per m^3 concrete. The results given in Lay et al.[22] (see Fig. 4.13), reveal that in the practical relevant domain the cement paste volume has no significant effect upon the chloride diffusion coefficient, regardless of the binder type.



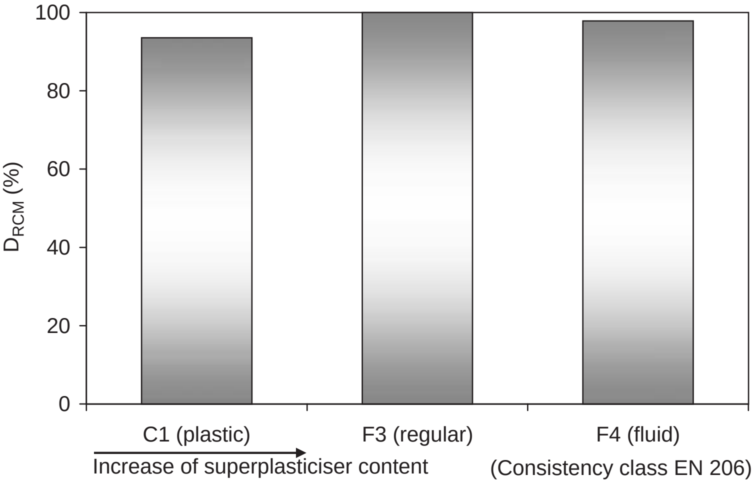
4.13 Influence of cement content on chloride diffusion coefficient. The effect is below the indicated limit of 20 %, regarded as significant[22].

4.3.9 Effect of air entrainment on the chloride diffusion coefficient

Entrained air increases the resistance towards frost-thaw. In Tang and Utgennant[23] concrete without or with (4.5 %) air entrainment was exposed in the road environment and tested after around 2 years of exposure for chloride profiles. No effect upon the apparent diffusion coefficient D_{app}, which was fitted from these chloride profiles, was observed. In Lay et al., 2003[22] concretes (OPC, w/b = 0.45) with air void volumes of 0.33 % (without air entrainment), 6 % and 10 % (with air entrainment) were investigated. An increase in air void volume resulted in a steady reduction of only a maximum 4 % in chloride migration coefficient D_{RCM}. Compared with the reproducibility of the test procedure this reduction can be considered as negligible.

4.3.10 Effect of superplasticiser content on the chloride diffusion coefficient

In Lay et al.[22] concrete (OPC, w/b = 0.45) was first produced without addition of a superplasticiser and the consistency was determined. Subsequently a superplasticiser (melamin–napthalinsulfonat) was added step-wise. After each addition the consistency was tested and specimens were prepared for chloride migration testing. The results indicate that in the investigated (practical) domain of 0.3–2.2 wt.-%cement the content of superplasticiser



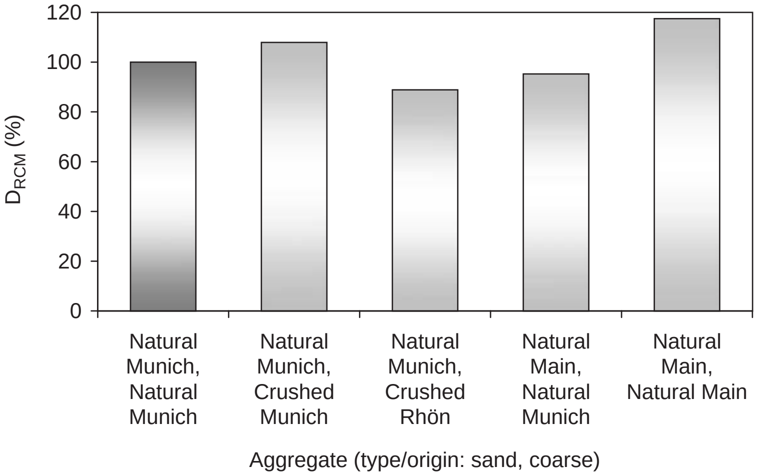
4.14 Influence of superplasticiser content (consistency class) upon chloride migration coefficient (360 kg/m^3 CEM I, w/b = 0.45) (Lay et al.[22]).

and the achieved consistencies between C1-F4 according to EN 206[24] have no influence upon the chloride diffusion properties (Fig. 4.14).

4.3.11 Effect of aggregate type and fineness on the chloride diffusion coefficient

Very few data are available on this topic. Care[25] tested mortars produced with sands of different fineness (coarse, medium, fine) with maximum grain diameters of 4, 2 and 1 mm respectively. With increasing fineness of the sand (at constant sand volume) the volume of the interfacial transition zone increased, causing an increase in the effective diffusion coefficient by the order of two when comparing coarse and fine aggregates.

In Lay et al.[22] the reference aggregate (natural gravel, Munich) was systematically exchanged by either crushed aggregate of the same gravel pit or aggregate from different regions (German Main or Rhön region). The grain size distribution of the three aggregate fractions 0–4, 4–8 and 8–16 mm conformed with the requirements set out by DIN-1045[24] to achieve a distribution A/B 0–16 mm. For crushed aggregate a higher diffusion coefficient may be expected as the volume portion of the interfacial zone is larger. The experimental results however show no clear trend nor any significant change in the diffusion properties when comparing natural and crushed aggregates. The same can be stated for the effect of the aggregate origin although natural aggregates with different porosity were used in the studies (Fig. 4.15).



4.15 Influence of aggregate type upon chloride migration coefficient (Lay et al.[22]).

4.3.12 Chloride diffusion coefficient: conclusion

In essence, the content of cement, superplasticiser and air voids as well as the aggregate type can be neglected, whereas the binder type, the w/b-ratio and the age of the concrete are very relevant regarding the chloride migration coefficient of concretes.

4.4 Chloride concentration

4.4.1 Concept

Especially in the case of an intermittent impact of chlorides on concrete structures, practical observations have shown that the application of Fick's second law of diffusion entails conditions. As already outlined above, close to the surface of a component, the concrete is exposed to a continuous cycle of wetting and subsequent evaporation. Here the water carrying dissolved chlorides moves in and out; this contradicts the assumption for diffusion where chlorides move within motionless water. This zone is here referred to as the 'convection-zone'. In order to describe the penetration of chlorides for intermittent loading with the 'error function solution' of Fick's second law of diffusion the convection zone Δx was introduced by Gehlen[3], which is the outer zone of the concrete cover where the transport process of chlorides is not diffusion controlled. Beyond the depth of the convection zone Δx, the effect of dispersion and diffusion may be described by a diffusion approach, for which the simple error function solution is again applicable. Instead of using the chloride concentration at the surface $C_{S,0}$, the starting point of the calculation with the error function solution is thus the depth Δx, where the concentration $C_{\Delta x}$ is considered to remain constant over time (see also Figure 4.4).

$$C(x,t) = C_i + (C_{\Delta x} - C_i)\cdot \mathrm{erf}\left(1 - \frac{x - \Delta x}{2\sqrt{(t - t_{exp})\cdot D_{app}(t)}}\right) \qquad [4.9]$$

where

$C(x,t)$ = chloride concentration at depth x at age t in e.g. [wt.-%cement]
C_i = initial chloride background level in e.g. [wt.-%cement]
$C_{\Delta x}$ = chloride content in depth Δx [wt.-%cement]
D_{app} = time dependent apparent diffusion coefficient [m^2/s]
t_{exp} = time until first exposure to chlorides [s]
t = concrete age [s]
erf = error function

When changing the concrete composition to enhance the resistance towards chloride ingress (reducing the chloride diffusion coefficient) it must be recognized that the concentration $C_{\Delta x}$ depends both on the environmental exposure and on the concrete composition, as will be discussed in the following section.

4.4.2 Effect of binder type upon chloride concentration

When using impermeable aggregates chlorides are only bound in the cement paste. As a consequence the type of binder has a significant influence on the surface concentration (Bamforth[26]). In structures exposed to a road environment in the UK a concentration of up to 0.75 wt.-%concrete was found for OPC, whereas concrete produced with fly ash or slag showed higher surface concentrations up to 0.9 wt.-%concrete. The same qualitative relation was found by Thomas and Bamforth[27] in marine splash conditions: After 8 years of exposure the observed surface concentrations were around 0.4, 0.5 and 0.53 wt.-%concrete for concrete produced with pure OPC, OPC with fly ash and additions or blending agents of slag respectively. The observable binder specific behaviour can be attributed to differences in the binding capacity caused by higher portions of aluminate phases (C_3A, $C_2(A,F)$) and/or the larger specific pore surface area.

4.4.3 Effect of binder content upon chloride concentration

According to Buenfeld and Okundi[28], the surface concentration C_0 increases with rising binder content. In ponding tests the surface concentration increased by around 30 to 40 %, when increasing the content of OPC from 300 to 450 kg/m^3 (w/b = 0.40–0.50). Concrete with 40 % fly ash or 75 % slag showed an increase of around 50 % for equal w/b ratios.

4.4.4 Effect of water–binder ratio upon chloride concentration

When using the total chloride content as a reference a linear relationship between surface concentration and w/b ratio was found in Frederiksen[29]. A change of the water–binder ratio of w/b = 0.3 to 0.7 resulted in an additional rise by about 130 % when using a Portland cement with high sulfate resistance at a constant cement paste volume of 27 V.-%. This led to the following relation:

$$C_{S,0} = 11 \cdot w/b\,[\text{wt.} - \%/\text{binder}] \text{ valid for } w/b = 0.3 \text{ to } 0.7 \qquad [4.10]$$

where

$C_{S,0}$ = chloride surface concentration [wt.-% binder]
w/b = water–binder ratio [–]

The results show that the effect of the w/b-ratio upon the surface concentration is by far lower than is the case upon the resistance towards ingress (diffusion coefficient). The relation given above can be assumed to be likewise applicable to the chloride concentration in the depth ΔX, $C_{\Delta X}$. Further systematic works on the effect of the w/b-ratio on the concentration $C_{\Delta X}$ when using different binder types are not known to the authors. However, this problem may be solved by using binding isotherms for estimation purposes as outlined in the following section.

4.4.5 Using binding isotherms for calibration upon chloride concentration

The effect of binder type, binder content and w/b-ratio can all be described by chloride binding isotherms. Chloride adsorption isotherms can be taken from literature data, as given for instance in Tang and Nilsson[30] or determined in the laboratory. The ratio of free chlorides to bound ones may be expressed by the so called ‘Freundlich-Isotherm’, involving binder type and porosity of the concrete:

$$c_b = f_b \cdot \frac{W_{Gel}}{1000 \cdot \varepsilon} \cdot c^{\beta} \qquad [4.11]$$

where

c_b = bound chlorides in cement paste [g/l]
f_b, β = regression parameters

W_{Gel} = cement paste content [kg/m^3]
ε = concrete porosity [$m^3_{pores}/m^3_{concrete}$]
c = concentration of solution (water) [g/l]

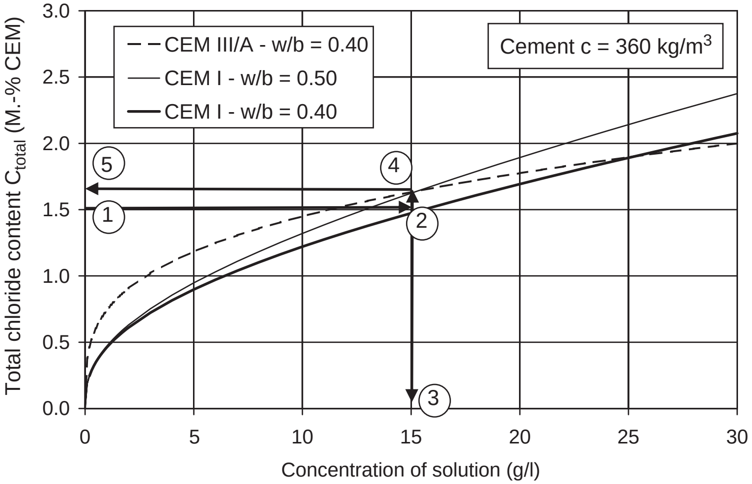
Binding isotherms can be used to estimate the surface concentration. For structures that are submerged or in constant contact with chloride-containing water the chloride concentration $C_{\Delta x}$ can be directly determined from binding isotherms. However, concrete surfaces that are not in constant contact with chloride-containing water as is the case for structures in the splash-zone of the sea or structures in the road environment, will show lower concentrations that depend on a number of environmental and geometrical influences. If the surface concentration in a certain environment is sufficiently quantified for a specific concrete composition, binding isotherms can be used to make an estimate on the expected surface concentration if a different concrete composition should be used. For example, if a concrete produced with 360 kg OPC and w/b = 0.40 shows a surface concentration of around 1.5 wt.-%concrete in a certain environment, the use of cement with additions of 50 % slag (CEM III/A) would lead to a value of around 1.66 wt.-%concrete according to the binding isotherms given in Table 4.5. A similar result is to be expected when changing the w/b ratio from 0.40 to 0.50 while all other parameters are kept equal, Fig. 4.16.

4.4.6 Further effects of concrete composition upon chloride concentration

Effects caused by aggregate type, admixtures as superplasticisers or air-entraining agents are considered as negligible though no experimental evidence is known to the authors.

Table 4.5 Parameters of chloride binding isotherm[30]

Binder type	f_b	β
100% CEM I (OPC)	3.57	0.38
30% slag + 70% CEM I	3.82	0.37
50% slag + 50% CEM I	5.87	0.29
30% fly ash + 70% CEM I	5.73	0.29



4.16 Using binding isotherms to estimate chloride surface concentration.

4.5 Critical chloride threshold

4.5.1 Dominating influences upon the chloride threshold value

Predictions on chloride-induced corrosion require a reliable chloride threshold value; otherwise there is no sense in improving the precision of predictions on chloride ingress by increasing the degree of sophistication. It has been widely recognised that there is no single threshold value for hardened concrete. The observed scatter in observations is enormous, which has caused rather conservative restrictions in the domain of 0.2–0.5 wt.-% cement. The lack of agreement is primarily due to the numerous influences upon chloride threshold value, which make comparisons of test results achieved with different test set-ups rather difficult.

The most important influencing interrelated parameters are summarised in Table 4.6, which is very similar to the excellent literature review of Glass and Buenfeld[31] but also includes updates on more recent investigations. The conclusions of the literature study by Glass and Buenfeld[31] were as follows:

- Chloride binding and pore solution pH are not major factors upon the threshold level.
- Weakly bound chlorides, i.e. those chlorides that can easily be set free again (e.g. by a change in pH) present a significant corrosion risk.
- The most important aspect affecting the threshold appears to be the condition at the steel–concrete interface. At the rebar surface dense

Table 4.6 Effect of various influences on chloride threshold with an increase in influence with indication of solely hypothetical (hyp) or experimental (exp) evidence, ↑: a rise in the regarded influence causes an increase of the threshold value

Influence	Effect	Evidence	Influence	Effect	Evidence
Theoretical			*Concrete cover*		
Cl^- binding	↑	hyp[32]	curing	–	exp[33]
Cl^- mobility	↓	hyp[34]	w/c	↓	exp[53]
Oxidizing conditions	↓	hyp[35]	cement content	↑	exp[37]
Steel interface			cover depth	↑	exp[53]
voids	↓↓	exp[36]	*External factors*		
pre-rusting	↓	exp[37]	moisture at low level	↓	exp[45]
steel composition		exp[38]	moisture at high level	↑	hyp[45]
half-cell potential	↓	exp[39]	moisture variations	↓	hyp[53]
surface roughness		exp[38]	oxygen concentration	↓	hyp
Binder			external chloride source	↓	hyp[40]
C_3A content	↑	hyp[41]	chloride type	–	hyp[42]
pH	↑	hyp[43]	temperature	↓	hyp[44]
FA	↓	exp[55]			
GGBFS	↓	exp[53]			
SF	↓	exp[50]			

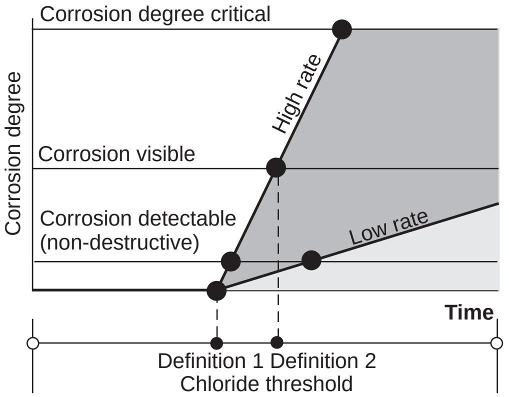
cement pastes accumulate providing homogenous conditions and a buffer of protective OH^-. Hence the threshold level is best presented as a total chloride content expressed relative to weight of cement, because it represents the total amount of aggressive substance (Cl^-) relative to the total potential corrosion-preventing substance (OH^-).

When comparing chloride threshold values care must be taken defining them. Basically two definitions for the chloride threshold are known:

- Definition 1: Chloride content at which depassivation of the steel surface begins, regardless of whether this causes (visible) corrosion damage.
- Definition 2: Chloride content which leads to deterioration or damage.

Apart from the depassivation of the steel surface further conditions must be met to induce corrosion rates that will lead to damage within the service life of a structure and therefore thresholds according to definition 2 are higher than those for definition 1.

It is a well-known fact that in constantly dry concrete (high resistivity) or water-saturated concrete (low oxygen availability) almost no reinforcement corrosion takes place. Under these circumstances much higher threshold values will be obtained when sticking to definition 2. Low threshold values will be observed at constantly humid or at alternating wet–dry

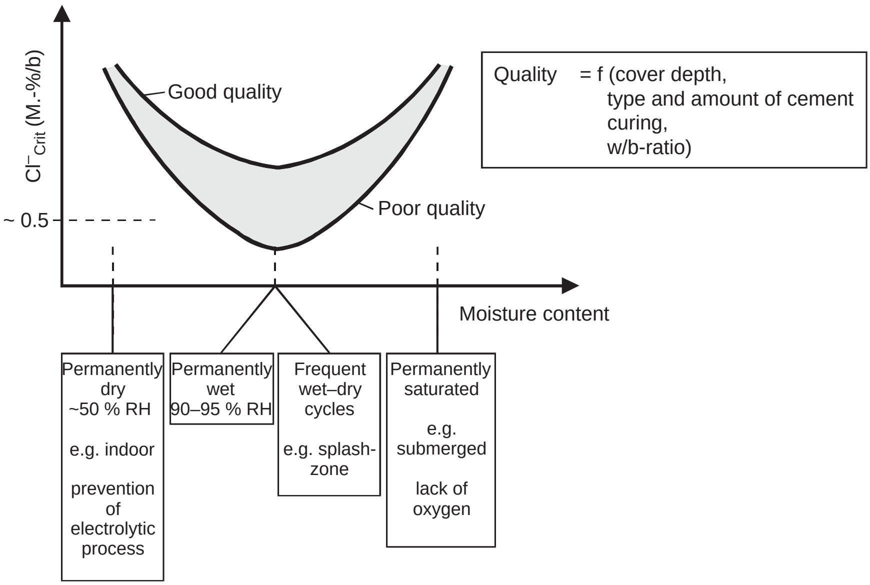


4.17 Definitions for chloride threshold.

conditions. The effect of relative air humidity on the chloride threshold was studied by Pettersson[45]. A minimum threshold was found at around 90 % RH for steel in mortar (w/c = 0.50, sulfate-resistant PC). A varying moisture state caused by wetting and drying of concrete has been found to result in substantially lower threshold values, see for instance Sandberg[51]. Here depassivation (definition 1) will also lead to visible corrosion damage (definition 2) within a short period. Regardless of which definition is chosen, it must be realised that detection of depassivation is only possible after the actual dissolution of the passive film layer has occurred. The measured threshold value will thus always be overestimated to a certain extent, Fig. 4.17.

The above relationships have been summarised by Schiessl[46], where the critical chloride content (definition 2) is considered to be mainly controlled by the moisture content and the quality of the concrete cover. A more stable micro-environment at the reinforcement as a result of an increased cover depth, lower w/b ratio and few micro-defects at the rebar surface (good concrete quality) will lead to higher thresholds compared to poor concrete quality under similar environmental conditions. These comparisons are summarised in Fig. 4.18.

Modern concrete structures should in consequence be built with a sufficiently low water to binder ratio and a large concrete cover, as these measures do not only increase the time for the chloride to reach the concrete but also minimise moisture and temperature variations at the steel–concrete interface and thus increase the chloride threshold. Systematic experimental evidence for these relationships are few, because testing of specimens with high cover depth is unfortunately very time consuming if the ingress of chlorides from the surface is to be studied.



4.18 Qualitative relationship of the critical chloride content, the environmental conditions and quality of concrete cover as given in *CEB Design Guide*[46].

4.5.2 Potential test methods

When designing test conditions the most relevant influences must be considered. These are:

- Composition of the pore solution (electrolyte).
- Mobility of ions within the surrounding electrolyte.
- Availability of oxygen.
- Voids (inhomogeneities) at the steel surface.

Thus the following test conditions can be listed (first list) in the order of increasing practical relevance. The second list deals with increasing uncertainty about the conditions at the steel surface.

- Tests of steel in artificial pore solution of known composition, aspect (a). In this respect the control of the Cl^-/OH^- ratio is an important issue, because Cl^- and OH^- ions compete for reaction sites at the steel surface.
- However, in concrete the mobility of ions is much lower than in electrolyte solutions, aspect (b). Thus specimens can be cast with low mortar or concrete cover to be stored under defined laboratory conditions.

- Finally, specimens can be tested under practical relevant conditions. This implies the aspect of oxygen availability (c), which depends on quality and thickness of concrete cover as well as on moisture conditions, and the realistic simulation of the conditions at the steel surface including the workmanship, aspect (d).

  Basically, four test conditions can be identified that aim to simulate practical conditions. Out of these none is solely capable of simulating the entire range of real field conditions[47].

(a) Field testing of laboratory cast concrete, with small covers (10–20 mm), with varying concrete composition (binder type, w/b-ratio), missing the effect of practical cover depth and variation in workmanship (especially compaction).
(b) Laboratory testing of reinforcement bars embedded with small covers (because of their appearance frequently called 'lolly-pop' specimens), usually under submerged conditions but sometimes with the environmental impact simulated by potentiostatic controlled steel potentials, missing the effect of cover, variable compaction and usually varying microclimate.
(c) Field testing of existing old structures, often with w/b >0.5 and OPC as binder, missing the effect of low w/b ratios and the effect of new binders.
(d) Laboratory or field exposure tests of concrete with chlorides in the mixing water, thereby allowing for the use of low w/b-ratios, thick cover depth and various binder types, missing the effect of steel passivation in chloride-free concrete and incorporating the effect of different chloride binding and hydration mechanisms when compared to subsequent penetrated chlorides. (This is the most erroneous method).

4.5.3 Results from tests under defined laboratory conditions

The results of Pettersson[48,49] and Hansson and Sørensen[50] were derived from studies of steel electrodes embedded in concrete submerged in chloride solution in the laboratory. They indicated that the time until depassivation depends on the binder type and the w/b-ratio, as could be expected because the diffusion coefficient is altered significantly. A significant influence of the binder type upon the chloride threshold value could not be proven. Breit[56] investigated the chloride threshold value in the laboratory by means of potential–current measurements on embedded steel electrodes, which were submerged in solutions of different Cl^-/OH^--ratios. Here again a significant influence of the concrete composition could not be found.

4.5.4 Results from tests under practical exposure conditions

Thomas[55] studied the rebar mass loss vs. the chloride content at bar location for various contents of fly ash in concrete exposed in a marine splash zone (Canada). As a criterion he defined a mass loss of 0.1 % at the rebar. For pure OPC he obtained a threshold of around 0.7 wt.-%/cement. An increase in fly ash portion of 15, 30 and 50 % caused a decrease in threshold by around 7, 30 and 70 % respectively.

Sandberg[51] exposed reinforced concrete slabs of different composition (binder, w/b-ratio) under variation of the concrete cover in a marine environment (field station Träslövsläge). The state of depassivation was determined by a combination of half-cell potential and polarisation resistance measurements. If depassivation was confirmed the total chloride content was determined at the vicinity of the reinforcement. From the total study Sandberg concluded that the chloride threshold value:

- Is about twice as high in submerged compared with marine splash conditions.
- Increases with rising cover depth (covers of 10–20 mm were tested).
- Increases for lower w/b-ratios (domain of 0.3–0.75 was tested).
- Is not significantly altered when using silica fume or fly ash instead of OPC, but may be reduced by the application of cement with high slag content.
- Is significantly raised, if voids >0.1 mm at the steel–concrete interface can be avoided (by good compaction).

Low threshold values for slag cements were mainly attributed to the higher sensitivity for the formation of air voids and micro-cracks (due to shrinkage) at the steel surface. The lower calcium hydroxide reservoir was also taken into consideration.

The effects of cover and w/b-ratio are mainly controlled by the induced moisture variations at the depth of the reinforcement. The effect of cover depth is assumed to be decisive until a depth of around 20 mm for concrete with w/b of around 0.40 and 55 mm for concrete with w/b of around 0.55. Beyond this depth changes in moisture content with time are thought to be of negligible importance.

4.5.5 The chloride threshold value: conclusions

The aspects of concrete composition and exposure environment were summarised during the widely recognised HETEK project headed by the Danish Road Directorate, Table 4.7. This table indicates that the threshold value decreases with incorporation of concrete additions or blending agents

Table 4.7 Thresholds in macro-crack free concrete in various marine or laboratory exposure regimes (see details above) based on work of Pettersson[45], Pettersson and Sandberg[52], Sandberg[53], Arup[54], Thomas[55] and Breit[56]. Test conditions (A, B and C) as outlined in Section 4.6.2

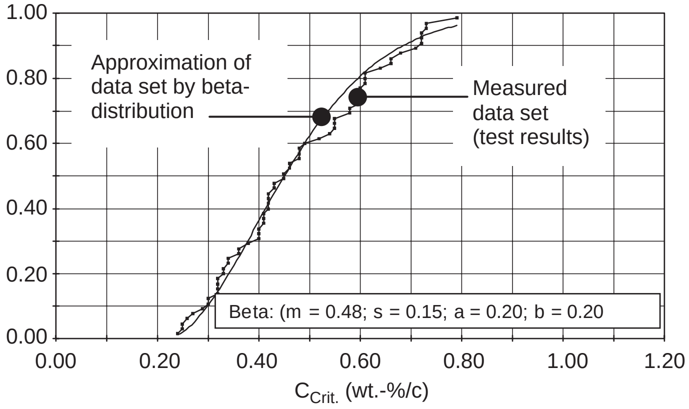
Binder	Submerged		Splash		Atmospheric	
	[wt.-%/cem]	Test	[wt.-%/cem]	Test	[wt.-%/cem]	Test
			w/b = 0.50			
CEM I	1.5–2.0	A	0.6–1.9	A		
CEM I	1.6–2.5	B	1.2–2.7	B	1.5–2.2	B
CEM I	>2.0	C	0.3–1.4	C		
5%SF	1.0–1.9	A				
5%SF	0.8–2.2	B				
20%FA			0.3–0.8	C		
			w/b = 0.40			
CEM I	>2.0	A	0.9–2.2	A		
CEM I	>2.2	B				
5%SF	>1.5	A				
CEM III/A			0.4–0.9	A		
			w/b = 0.30			
CEM I	>2.2	A	>1.5	A		
5%SF	>1.6	A	>1.0	A		
20%FA	1.4	A	0.7	A		

and increasing w/b-ratio. This is mainly attributable to an increase in ion mobility at high w/b-ratios.

The concept of a chloride threshold value implies the idea that a rapid increase in corrosion rate occurs at a particular value, which is not observed in reality. It must be realised that the chloride contamination must rather be understood as an increase in corrosion probability. This leads to the expression of the chloride threshold as a statistical distribution, reflected in Fig. 4.19.

Threshold values as given above in Table 4.7 are usually presented in different ways, determined by different methods and in general miss relevant information. A statistical analysis to provide input data is thus rather difficult. As outlined above, threshold values depend on the cover depth, where different micro-climates at the steel–concrete interface are produced. The data that constituted the basis for the values in Table 4.7 were usually determined with cover thickness below 25 mm. The values can also be used safely for higher cover depth, for which sufficient quantification is currently lacking.

In constantly wet (submerged) conditions the microclimatic conditions are more homogeneously distributed. This leads to a higher mean value and a relatively lower standard deviation. In the EU project DuraCrete[57] a standard deviation of 0.2 is proposed under these circumstances. For constantly



4.19 Probability distribution function of chloride threshold according to data given in Breit[56].

humid or frequently changing ambient conditions a proportionally higher standard deviation of 0.1 (for w/b 0.40 and 0.50) and 0.15 (for w/b = 0.30) is proposed.

It should be realised that the above proposed figures reflect the currently best available knowledge. However, it is still necessary to carry out well-planned research to link clearly the dependence between the concrete specific threshold values and the environmental exposure conditions. Moreover, it should be kept in mind that the steel–concrete interface is still considered as the overwhelming influence on the threshold level, which is to a large extent dependent on the workmanship. An appropriate characterisation and, more importantly, a prediction of this key parameter seems currently out of reach. A good quality insurance system is thus necessary to keep the real threshold values in the expected domain.

4.6 Corrosion rate

4.6.1 General

As already detailed in Chapters 1 and 3, the electrolytic resistivity of the concrete is a major and currently the only well-investigated parameter with respect to the active corrosion phase. All further explanations on the dependence of the corrosion rate upon the concrete composition are thus focused on this decisive parameter. The electrical resistivity (the inverse is referred to as conductivity) of a material is the resistance towards transmittance of a continuously and uniformly distributed electrical current in a volume with length L and constant cross-sectional area A:

$$\rho = \frac{A \cdot R}{L} \qquad [4.12]$$

where

ρ = resistivity [Ω m]
A = cross-sectional area [m^2]
R = resistance [Ω]
L = length of conduction path [Ω]

The most common units for resistivity are kΩ cm or Ω m. Various methods for measurement in laboratory or *in-situ* have been developed in the past. Generally measurement is conducted by means of alternating current techniques (AC) at low frequencies in order to avoid polarisation effects induced by direct current measurement.

4.6.2 Effect of binder type

At the beginning of the hydration most of the mixing water and the dissolved ions are available as an electrolyte for the current transport. As the hydration progresses the amount of free water in the pore structure is reduced. With increasing degree of hydration the electrolytic resistivity of concrete also increases. This time-dependent development differs widely for the various existing binder types.

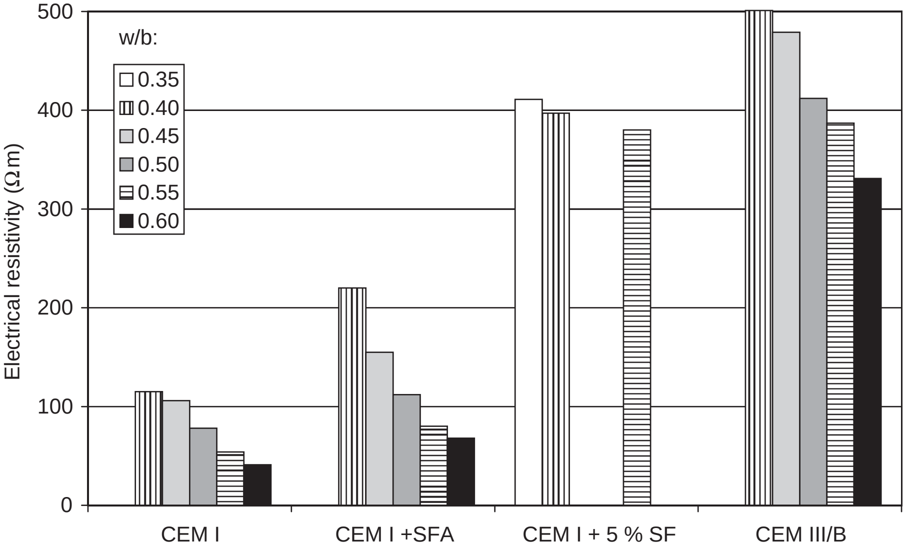
4.6.2.1 Effect of fly ash, slag and silica fume

Electrical resistivity of concrete with fly ash is much higher compared to that of OPC. At an age of 28 days the resistivity of concrete produced with w/b-ratios from 0.40 to 0.60 is around 330–550 Ω m for slag cements (CEM III), 380–410 Ω m for cement with silica fume, 70–220 for cements with fly ash in comparison with 40–114 Ω m for OPC[58,59,60,61,62,63,65].

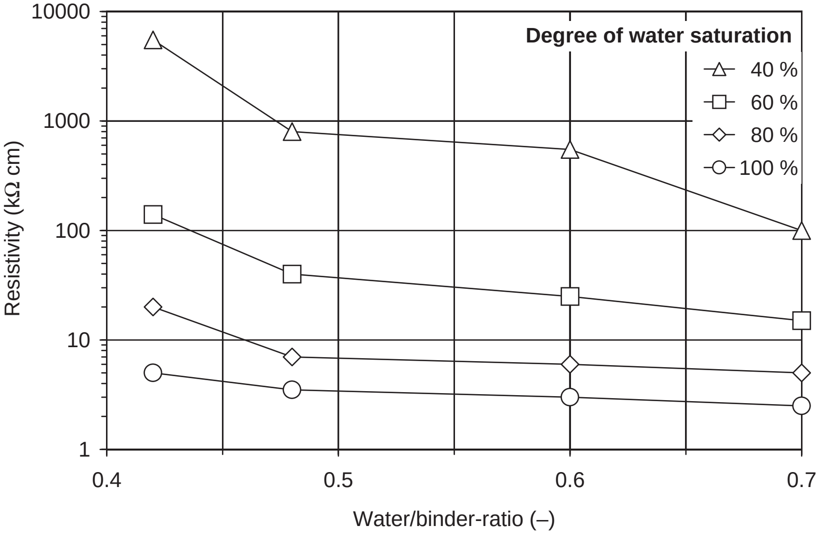
A significant increase of resistivity with silica fume content was found by Berke et al.[64]. The rate of increase of resistivity with time is very high for concrete produced with additions of fly ash or slag. The hydration and thus the increase in resistivity of such concrete proceeds for a much longer time in comparison with OPC, with or without additions of silica fume. During the proceeding hydration the resistivity tends towards a finite end value[56,65].

4.6.3 Effect of water–binder-ratio

The electrolytic resistivity of concrete decreases with increasing w/b-ratio in an exponential manner (see Fig. 4.20). In water-saturated concrete the effect of w/b-ratio is less significant in comparison with those conditions where concrete is allowed to dry out, which has been demonstrated by Gjørv et al.[66]. A reduction in water saturation causes a more pronounced increase in resistivity at low in comparison with that in high w/b-ratios, Fig. 4.21.



4.20 Electrolytic resistivity of concrete with different binder types and w/b-ratios at an age of 28 d under water saturation (20 °C), Gehlen[3].



4.21 Effect of water saturation and w/b-ratio on electrolytic resistivity (OPC). Data from Gjørv et al.[66].

4.6.4 Effect of binder content

The electrolytic resistivity is dominated by paste characteristics and a change of binder content for a constant w/b-ratio will therefore cause a change in resistivity. Measurements by Hughes et al.[67], showed a slight decrease in resistivity with increasing cement content.

4.6.5 Effect of aggregate type

There are enormous differences in resistivity observable for different aggregate types. However, no specific studies on the effect of aggregate type on the electrical resistivity of concrete are available. It is to be expected that concrete produced with denser aggregate (such as granite) will show higher resistivity than does concrete with rather porous aggregate (such as sandstone). The resistivity of a multi-component material is always dominated by the most conductive material, which is the cement paste in the case of concrete. The more conductive the cement paste (e.g. high w/b-ratio, early age) the lesser the influence of the aggregate type. In a typical concrete mix (OPC, $w/c = 0.45$, 28 days of age) under water-saturated conditions the effect of a change from very porous to very dense aggregate is expected to be around a factor of <2.

4.6.6 Further effects of concrete composition

The authors know of no systematic investigations for the electric resistivity concerning the effect of such admixtures as air entrainment or superplasticisers. Within the practical domain these influences must be considered as negligible; this has already been proved for other comparable properties such as chloride ingress resistance.

4.7 Recommendations for the use of concrete made of modified cements

Regarding the process of carbonation the use of fly ash and moderate contents of silica fume will enhance the carbonation resistance, while concretes produced with large contents of blast furnace slag will show a significant reduction in carbonation resistance. With respect to the chloride penetration resistance the use of fly ash, silica fume and blast furnace slag will always improve the resistance, due to the refined pore structure. Application of limestone-blended cements will always reduce the ingress resistance either of the carbonation or chloride front. Looking at the overall process of reinforcement corrosion (depassivation and propagation phase) the use of blended cements must always be regarded as beneficial. However, care must be taken that sufficient curing is provided for cements with additions of fly ash and blast furnace slag. Moreover, other deterioration mechanisms such as frost or de-icing salt attack must always be recognized; for these cements, in general, provide lower resistance.

4.8 List of frequently used abbreviations and symbols

Abbreviations

ACC	Accelerated carbonation
FA	Fly ash
GGBFS	Ground granulated blast-furnace slag
OPC	Ordinary Portland cement (CEM I according to European standardisation)
RCM	Rapid chloride migration
SF	Silica fume

Symbols

$C_{\Delta x}$	Concentration in depth of convection zone
C_{Crit}	Critical chloride threshold
D_{app}	Apparent diffusion coefficient
D_{eff}	Effective diffusion coefficient
D_{RCM}	Rapid chloride migration coefficient
Δ_x	Depth of convection zone
R_{ACC}	Carbonation resistance measured under accelerated conditions

4.9 Sources of further information and advice

The *Bulletin d'Information* No. 148 entitled 'Durability of concrete structures, state-of-the-art report'[68] is a rather complete compendium on durability aspects, published in 1982. In the second phase within the Comité Euro International du Béton a practical guide for the durability design was introduced called CEB Bulletin No. 182 'Design Guide for Durable Concrete Structures'[69] which still is an important source of information. A general approach for a probabilistic durability design comparable with the structural design procedure was also elaborated in CEB, finally leading to the CEB Bulletin No. 238[70]. This was the basis for the EU research project DuraCrete, finished in 1999. It provided a probabilistic design framework and models including the necessary quantification for various deterioration mechanisms that were based on a sound review of the state of the art; only a few reports can be mentioned here[71,72]. Besides being disseminated in the

DuraNet network[73] the DuraCrete ideas have recently also been incorporated into concepts for existing structures. In this respect, EU projects such as LIFECON[74], CONTECVET (see the website[75]), EUROLIFEFORM[76] and DARTS (Durable And Reliable Tunnel Structures)[77] should be mentioned as important sources of further information.

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5

Stainless steel in concrete structures

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5.1 Stainless steel reinforcement

5.1.1 Introduction

Steel in concrete is usually protected against corrosion by passivation of the steel arising from the high alkalinity of the pore solutions within the concrete. A stable oxide layer is formed on the steel surface which prevents the anodic dissolution of iron. Loss of durability in reinforced concrete only occurs if this oxide layer is rendered unstable (if depassivation occurs) due to the ingress of chlorides to the steel–concrete interface or carbonation of the concrete reducing the alkalinity of the pore solution in the hardened cement paste around the steel. Durable reinforced concrete therefore must be designed to resist carbonation and to exclude chlorides from any source.

Reinforcing steel should be embedded in concrete specified in accordance with current standards. In particular the mix design and minimum cover must be observed and be suitable for the corrosivity of environment. In many cases this will provide sufficient corrosion protection to the reinforcing steel, provided that the concrete is correctly placed, compacted and cured.

Nevertheless, there is significant evidence that some of these conditions are not fulfilled and that problems of steel and concrete deterioration are due either to inadequate design or to incorrect site practice. There are circumstances in which it is difficult to achieve the specified design life without additional corrosion protection measures. Problems arise if:

- Structures are exposed to high concentrations of chlorides (e.g. in marine structures and bridge or parking decks due to the use of deicing salts).
- The concrete cover and the concrete quality is, by design or otherwise, reduced relative to the necessary values for the surrounding environmental conditions (e.g. in extremely slender elements).

- Special structures have to be built, e.g. connections between precast and cast-in-place elements or heat-insulated joints between the structure and external structural elements (e.g. balconies).
- Non-dense or dense lightweight concrete is designed to reach a required thermal insulation as well as low ownweight.
- Access to the structure is strongly limited, making future inspection and maintenance costly, such as in underground structures in aggressive soil.
- Future maintenance is possible but may cause extreme indirect costs due to non-availability, such as in bridges in the main traffic arteries of densely populated areas.

In such cases designers may consider modifications to the concrete mix design in order to decrease permeability. Additional corrosion protection measures such as coatings and surface treatments to limit chloride ingress into the concrete, the use of corrosion protected reinforcement and of materials that are more corrosion resistant for the reinforcement (e.g. galvanised steel or stainless steels), addition of inhibitors to the fresh concrete and cathodic prevention by impressed current may each be an economical and technically attractive approach. This chapter surveys modern aspects of the application of stainless steel reinforcement[1,2,3,4] that prevent or retard rebar corrosion and which are proposed and used for new reinforced concrete structures.

The term stainless steel does not refer to a single specific material but rather to a group of corrosion-resistant steels containing a minimum of 12 % chromium. Various alloying additions (nickel, molybdenum, nitrogen, titanium and others) may be added to provide, depending on composition, different mechanical and corrosion properties, weldability and other properties in service. With respect to microstructure, stainless steel reinforcement can be distinguished in ferritic, austenitic and ferritic–austenitic steels. Interest in the use of these alloys as reinforcing steel for concrete is due to their increased resistance to corrosion particularly in chloride-containing media. The decision on which of these types of stainless steel is the most suitable depends on:

- The degree of corrosion protection required.
- Cost aspects.
- Workability and application characteristics (mechanical properties, weldability).

5.1.2 Production and performance characteristics

Much of the information in this section is derived from two works by Nürnberger[2,4]. In principle, manufacture of stainless steel reinforcement by hot and cold deforming does not distinguish from production of mild steel reinforcement. Another development, which can significantly reduce the cost, involves producing a stainless steel clad reinforcement. In this approach, a core of ordinary steel is encapsulated in a stainless steel sheath to resist corrosion.

Ferritic steels in the as-rolled condition have a higher yield strength than do austenitic steels. There is a high probability that the bars may be further strengthened by cold twisting or cold rolling and these processes can be facilitated by employing a special alloy composition. In this process, the carbon and nitrogen contents are limited to avoid hardening after cooling from the austenite phase. The steel retains sufficient strength after cold deforming up to 12 mm diameter.

Acceptable high yield reinforcing bar strengths can be obtained from austenitic stainless steels. While there are other means of increasing the strength of austenitic stainless steels such as cold working (drawing and rolling, twisting) for the bars of lower diameter (e.g. 4 to 14 mm), a further attractive method is warm working. Warm working is extremely successful in increasing strength levels of small bars (<12 mm). An effective solution for large diameter bars up to 40 mm is the combination of using a modified composition (an addition of 0.15/0.20 % nitrogen) and the warm working process. Owing to their excellent mechanical properties in the as-rolled condition, duplex stainless steels are of interest as materials for reinforcements. In Germany such wires are cold deformed, in Italy they are as-rolled and cold deformed.

For application in concrete structures ferritic, austenitic and ferritic–austenitic steels can be produced as ribbed bars within the normal range of strength and ductility requirements. Such bars can be welded as part of normal construction practice. They fulfil the basic property requirements for reinforcing (mild) steel. Resistance welding is the most widely used welding method in factories. For instance, it is used for prefabrication of mesh reinforcement. MIG/MAG welding is the most frequently used method for welding carried out on site. In the construction practice, the welds are normally embedded in concrete without any subsequent treatment such as pickling or grinding.

The coefficients of thermal expansion of ferritic steel and concrete are approximately the same (1.2 and $1.0 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$ respectively). In comparison, the coefficient of thermal expansion of austenitic stainless steel is higher ($1.8 \times 10^{-5}\,^{\circ}\mathrm{C}^{-1}$). If a concrete structure with austenitic reinforcement is exposed to high temperatures, tensile stresses will be produced in the uncracked concrete as a consequence of the different thermal coefficients of steel and concrete. This may in theory cause some minor defects in the contact zone and expansion cracking, particularly in heavily reinforced sections. However, there is no practical evidence or laboratory results supporting this assumption.

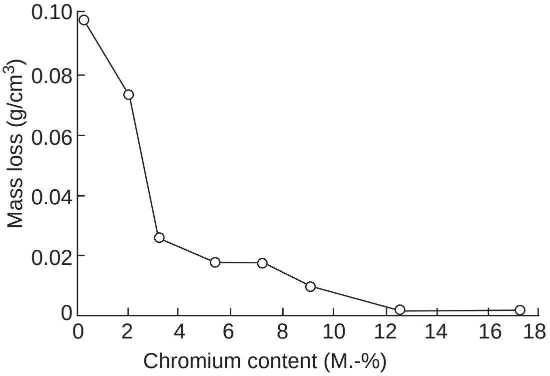
5.1.3 Corrosion behaviour

5.1.3.1 General aspects

Both Nürnberger[4] and Edelstahl-Vereinigung[5] have written on the general aspects of steel grades. Stainless steels are high alloyed steels, which in contrast to unalloyed steels do not show general corrosion and noticeable rust formation in normal environmental conditions (atmosphere, humidity) nor in aqueous, nearly neutral to alkaline solutions. A basic requirement for the above reaction is a minimum concentration in the steel of a particular alloying element and the existence of an oxidising agent (e.g. oxygen) in the surrounding medium; this causes passivation of the surface. 'Passivity' describes a condition that produces a strong inhibition of the reaction of protecting iron by forming a passive layer on the surface. Chromium, in particular, is an element that allows passivation. This property is transmitted when iron is changed to steel through alloying: general corrosion decreases in corrosion-promoting media in inverse relation to the content of chromium (see Fig. 5.1). The content of chromium that causes passivity when exceeded depends on the attacking agent. The content of chromium in water and in the atmosphere should at least be 12 M.-%. Corrosion resistance may be further improved by addition of such substances as nickel, molybdenum and nitrogen. Chromium, molybdenum and nitrogen are important elements in relation to pitting corrosion and nickel especially increases corrosion resistance in acid media.

5.1.3.2 Steel grades

Added elements, if present at a sufficiently high level, change the structure of the metal, the corrosion behaviour and other performance characteristics that are structure dependent. In common conditions that prevail in con-



5.1 Corrosion of chromium steels in industrial air[3].

struction engineering (attack by light acid or light alkaline aqueous media), ferritic steels with about 11 to 17 M.-% of chromium have a sufficient resistivity against general corrosion. With addition of sufficient chromium and molybdenum up to about 2 M.-%, resistivity against pitting corrosion can also be achieved. In addition, ferrites have a high resistivity to stress corrosion cracking in an environment containing chlorides. Above all, if there are comparable contents of chromium, the resistance of ferritic steels towards crevice corrosion is much enhanced over what it is for instance in austenitic steels.

Austenitic steels have at least 17 to 18 M.-% of chromium and 8 M.-% of nickel. These steels are especially used because of their positive corrosion properties and their superior workability in comparison with other stainless steels. Where there is the correct content of alloy, they have a high resistivity to general corrosion, pitting corrosion and crevice corrosion, but are sensitive to stress corrosion cracking in their typical state with about 10 M.-% of nickel. The resistance to pitting corrosion, crevice corrosion and stress corrosion cracking can be improved with the addition of chromium, molybdenum and nickel.

Ferritic–austenitic steels have a binary structure of ferrite and austenite. The typical range of their chemical analysis is 22 to 28 M.-% of chromium and 4 to 8 M.-% of nickel. Molybdenum can be added in order to improve the corrosion resistivity. These steels combine good properties of ferritic steels (high yield strength) and austenitc steels (good ductility, improved anti-corrosion properties).

Martensitic steels with an analysis similar to that of ferritic steels, but with an enhanced content of carbon, are distinguished from all other stainless steels by a substantially higher hardness and strength. Because of that, the usual carbon martensites are especially sensitive to hydrogen-assisted stress corrosion cracking. However, through a limitation of the content of carbon to a maximum of 0.05 M.-% and the addition of up to 5 % of nickel, the reaction towards stress corrosion cracking of these 'soft martensites' can be considerably improved. Assuming a comparable content of chromium and molybdenum and an equal surface quality, the classification of these materials is similar to that of ferritic steels in regard to corrosion.

The steel grades mentioned above are basically chosen with regard to their resistivity in the attacking medium, but particular technological characteristics are also considered with regard to processing and application. For economic reasons, the concentration of alloy should not be too high, but neither be too low considering the intended application conditions, so as to achieve the necessary resistivity in the attacking medium. For particular types of corrosion, e.g. pitting corrosion and stress corrosion cracking, the existence of a passive layer is a necessary requirement. Because of that, passive steels are resistant against general corrosion, but are sensitive to local corrosion in the presence of specific media (e.g. chloride ions) in the case of an insufficient content of alloy.

5.1.3.3 Types of corrosion

There are four types of corrosion of stainless steels: general corrosion, intergranular corrosion, stress corrosion cracking and pitting corrosion. The performance of the different stainless steels is now considered in relation to these corrosion types.

General corrosion

General corrosion takes place only if the medium is sufficiently acid. The lower the pH value and the higher the temperature, the more difficult it is to achieve passivation. Under such conditions the steel must have a higher content of particular alloying elements in order to reduce a corrosion wastage or to achieve passivity. It is important that (at atmospheric corrosion) the corrosion rate in the active state decreases considerably if there is an increasing pH value. Corrosion resistivity generally exists above pH 4. Therefore, in weakly acidic media, in the usual atmospheric conditions and especially in alkaline media, chromium steels with >12 M.-% of chromium and all higher alloyed steels are passive. Therefore, a passivated steel cannot corrode in a medium such as concrete. The passive film is also stable if the concrete is carbonated[6].

Intergranular corrosion

Intergranular corrosion can only occur as the result of certain structural changes that may arise due to the welding process. All stainless steels are now specially alloyed to avoid this problem.

Stress corrosion cracking

Stress corrosion cracking can occur when the appropriate factors such as suitable material, specific environment and stress levels are present. As the tendency to stress corrosion normally increases with increasing chloride content, increasing temperature and decreasing pH value, this form of attack is unlikely to be a problem in concrete but is more likely to occur under atmospheric corrosion conditions (see Section 5.2). Stress corrosion cracking is also more likely to occur in welded structures when these are present in carbonated concrete with extreme amounts of chloride at higher temperatures. Nevertheless, stress corrosion cracking was not observed in any research described by Nürnberger[2].

Resistivity of stainless steels to chlorine-assisted stress corrosion cracking decreases in the following order: ferritic chromium steels, ferritic–austenitic steels, austenitic chromium–nickel (molybdenum) steels. This can be explained by the influence of the content of nickel on the sensitivity of those steels that contain a high proportion of chromium, to stress corrosion cracking. A minimum resistivity exists at about 10 M.-% of nickel. After this minimum, resistivity decreases depending on rising or decreasing content of nickel. In martensitic stainless steels, the reaction towards hydrogen-assisted stress corrosion cracking is decisive[7].

Pitting corrosion[2]

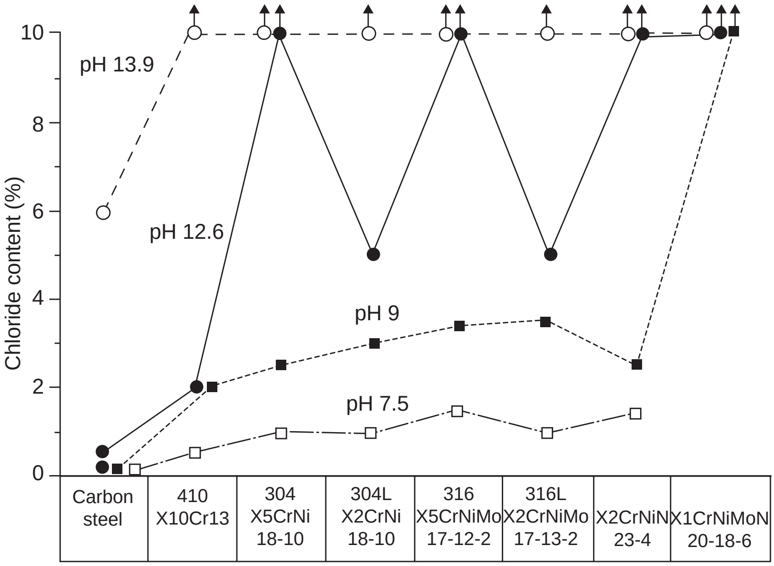
Pitting corrosion is the most common form of corrosion of stainless steels in concrete.

General aspects[4,5]

In pitting corrosion an interaction between chloride ions and the passive layer develops; in this the passive layer is locally interrupted and a pit expansion occurs after the depassivation. Crevice corrosion is an intensified pitting corrosion running down in crevices. Crevice corrosion occurs whenever structural elements are in some degree of narrow contact with each other and crevices develop (see Fig. 5.8). Here there can be a concentration of chloride ions below the corrosion products in the crevice and a decrease of the pH value as a result of a hydrolysis of the corrosion products. Because of that, corrosion in crevices occurs at even lower corrosion exposure than does pitting corrosion in areas that are free of crevices.

The tendency towards both pitting corrosion and crevice corrosion decreases depending on decreasing content of chloride, decreasing temperature and rising pH values. Acid chloride enriched media are therefore particularly critical. The adverse effect of decreasing pH value on the critical chloride content as a function of stainless steel composition is shown in Fig. 5.2. Tests in solutions simulating the alkaline and carbonated concrete pore liquid showed that stainless steels, although still passive, have a lower resistance to chloride-induced corrosion than in chloride containing alkaline solutions. The critical chloride concentration decreased especially for steels with low chromium content (X 10 Cr 13). Because of that, stainless steels are basically more resistant in concrete constructions where there are pH values of about 8 to 13 than they are, for instance, in atmospheric weather conditions. As a result, the standards for reinforcing steels and other structures such as anchorage devices in concrete are normally more modest than they are for structural elements in the open atmosphere.

Corrosion resistivity in media that generate pitting corrosion further depends on steel composition as well as on surface condition. Pitting



5.2 Critical chloride content in pH 7.5–13.9 solutions at 20 °C during potentiostatic tests at +200 mV vs. SCE[8] (chloride content in M.-%).

Table 5.1 Some commercially available standard grades of steel (source: according to European Standard codes as given in EN 10088)

Steel		Microstructure	PRE
1.4003	X2CrNi12	Ferritic	11
1.4301	X5CrNi 18-10	Austenitic	18
1.4541	X6CrNiTi 18-10	Austenitic	18
1.4401	X5CrNiMo 17-12-2	Austenitic	24
1.4571	X6CrNiMoTi 17-12-2	Austenitic	24
1.4462	X2CrNiMoN 22-5-3	Ferritic–austenitic	34
1.4539	X1NiCrMoCuN 25-20-5	Austenitic	38
1.4529	X1NiCrMoCuN 25-20-7	Austenitic	42

corrosion and crevice corrosion are especially influenced by the alloying elements chromium, nickel, molybdenum and further nitrogen. The susceptibility to pitting and crevice corrosion increases with the decrease of the so-called 'pitting resistance equivalent (PRE) number' (1 × %Cr + 3.3 × %Mo + 16 × % N) and decreases in the order Cr–Ni–Mo steel, Cr–Ni steel, Cr steel. Examples of commercially available standard grades, that can be used in air and concrete, and their pitting resistance equivalent are shown in Table 5.1 (the numbers follow European Standard codes as given in EN 10088). Nickel improves the corrosion resistance under conditions of crevice corrosion, because it raises resistivity to acid. Improvement takes place in the following order: scaled, raw grinded, blasted, fine grinded, pickled, polished.

Weld joints are more exposed to the danger of pitting corrosion than are similar non-welded steels, since oxide films (temper colours) or scale layers have developed in the weld joint area during the welding, because of incomplete or lack of gas metal arc. At an increasing thickness, these layers restrain passivation. The presence of welding scale and temper colours reduces passivity and can aggravate susceptibility to pitting corrosion if it is not removed. Furthermore, welding decreases the chloride threshold value for initiation of corrosion and it can destroy the low cathodic activity of stainless steel. In several cases this problem can be solved by pickling or shot blasting the weld. Pickling is, however, not a practical solution in industrial fabrication involving onsite welding of stainless steel.

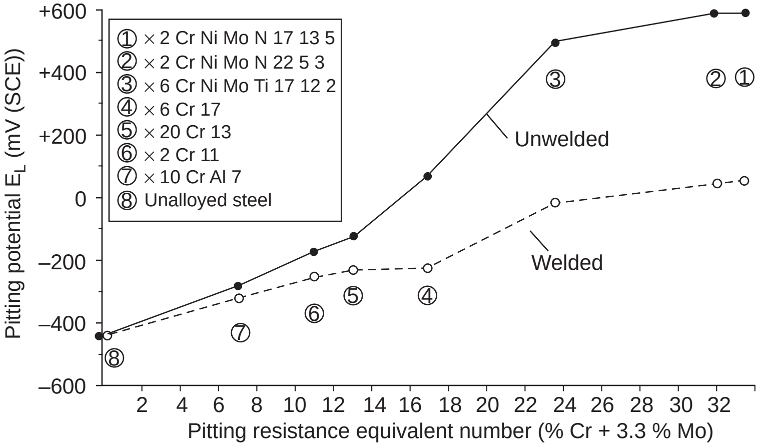
Electrochemical laboratory studies on stainless steel reinforcement

Many researchers have examined the performance of stainless steel reinforcement in electrochemical laboratory studies or in long term exposure programmes under severe marine or simulated marine conditions[2]. In comparison with mild steel bars, unwelded and welded stainless steel bars of the materials listed below were embedded in concrete of medium or poor quality and were exposed to seawater or chloride-containing solutions. The materials in question are the following:

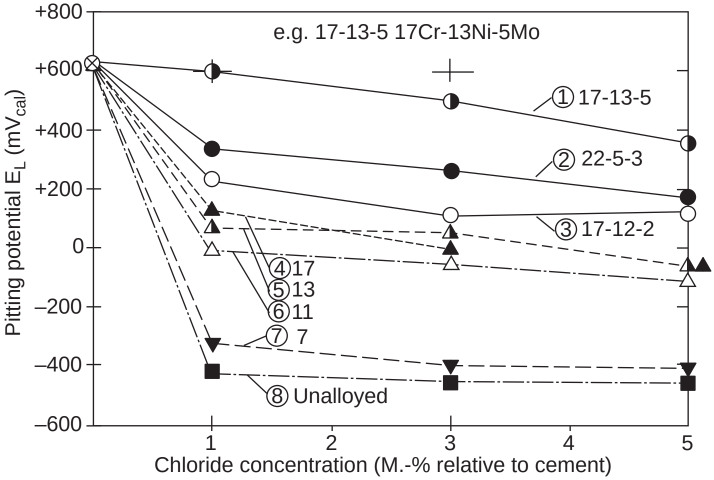
- Ferritic steel (chromium alloy steel), e.g. X2Cr11 (1.4003)[6,9,10,11].
- Austenitic steel (chromium–nickel alloy steel), e.g. X6CrNiTi 18-10 (1.4541) and austenitic steel (chromium–nickel–molybdenum alloy steel), e.g. X6CrNiMoTi 17-12-2 (1.4571)[6,9,11,12].
- Ferritic–austenitic steel (chromium, nickel, nitrogen alloy steel), e.g. X2CrNiN 23-4, ferritic–austenitic steel (chromium, nickel, molybdenum, nitrogen alloy steel), e.g. X2CrNiMoN 22-5-3 (1.4462)[6,13].

Figure 5.3 gives a short impression of the very different behaviour of unwelded and welded steels. The pitting potential of the welded specimens becomes more negative, but the difference between unwelded and welded steels decreases with decreasing chromium and molybdenum.

Figure 5.4 shows results of potentiostatic electrochemical tests using mortar specimens with unribbed steel bars. It shows the pitting potential of stainless steels and one unalloyed steel in the welded state in alkaline concrete with respect to the chloride content. The numbers beside the pitting potential versus chloride concentration curves refer to the content of chromium, nickel and molybdenum. Based on these and further test results the following important conclusions can be drawn:



5.3 Pitting potential of steel specimens with plain surface in saturated $Ca(OH)_2$ solution with 5 M.-% chloride (potentiokinetic tests)[6].



5.4 Pitting potential of plain welded steel specimens in PC mortar (potentiostatic test)[6].

- The pitting potential decreases with decreasing content of alloying elements.
- Three main groups can be indentified:
  - the austenitic and ferritic–austenitic steels 1 to 3 with the highest corrosion resistance;

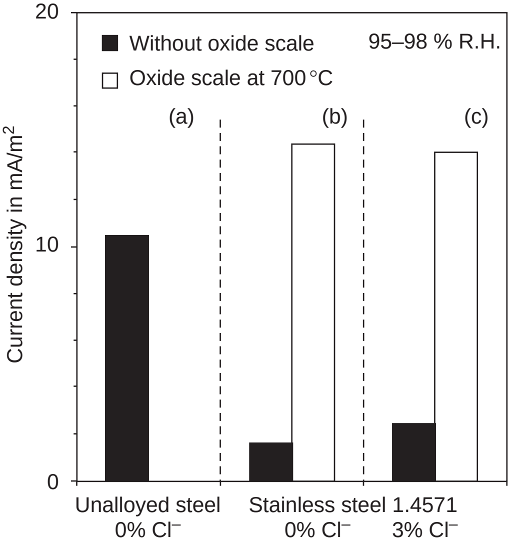
  - the ferritic types material 4 to 6 with chromium contents higher than 10 % in a middle range;
  - the ferritic types material 7 and 8 with chromium lower than 10 % and a low corrosion resistance, comparable to unalloyed steels.
- As expected, the pitting corrosion potential decreases with increasing chloride content of the concrete.

In carbonated concrete with chlorides, i.e. conditions which, for instance, may often occur for lightweight concrete or cracked concrete contaminated with deicing salts, the pitting potential is always shifted in the direction of more negative values in comparison with alkaline concrete with the same amount of chlorides.

Because of the very high cost of stainless steel reinforcement it is not likely that the entire reinforcement, for example in a large marine structure, would be made of stainless steel; it is possible that stainless steel would be used only as the outer reinforcement in the splash zone. Stainless steel and unalloyed steel will then probably be in electrical contact and this could lead to a theoretical risk of galvanic corrosion. As long as both metals are in the passive state their potentials will be approximately the same when embedded in concrete. Even if there should be minor differences in potential, both black and stainless steels can be polarised significantly without serious risk of corrosion, i.e., their potentials will approach a common value without the passage of significant current.

In situations where the unalloyed reinforcement is corroding and the stainless steel is passive, the galvanic coupling will give rise to accelerated corrosion. However, the coupling of corroding carbon steel with stainless steel is generally without risk and is negligible compared to coupling to passive carbon steel which always surrounds the corroding area[14–16]. Figure 5.5 shows that the macrocouple current density was almost one order of magnitude lower when corroding unalloyed steel in 3 % Cl^- concrete was connected with passive stainless steel, compared to the current density measured during the tests with a passive bar of carbon steel. Stainless steel has a higher overvoltage for cathodic reaction of oxygen reduction with respect to carbon steel. Therefore, the increase in corrosion rate on carbon steel embedded in chloride-contaminated concrete due to galvanic coupling with stainless steel is significantly lower than the increase brought about with passive carbon steel. Nevertheless, worse behaviour was observed in the presence of a welding scale (see Fig. 5.5). Its contribution to the macrocouple current is similar to or higher than that of carbon steel.

The macrocouple current density produced by austenitic stainless steels 1.4301 and 1.4401, coupled with corroding carbon steel in chloride contaminated concrete, increases as their yield strength increases and it is higher for the 1.4301 steel[17]. Nevertheless, the contribution of these steels to the



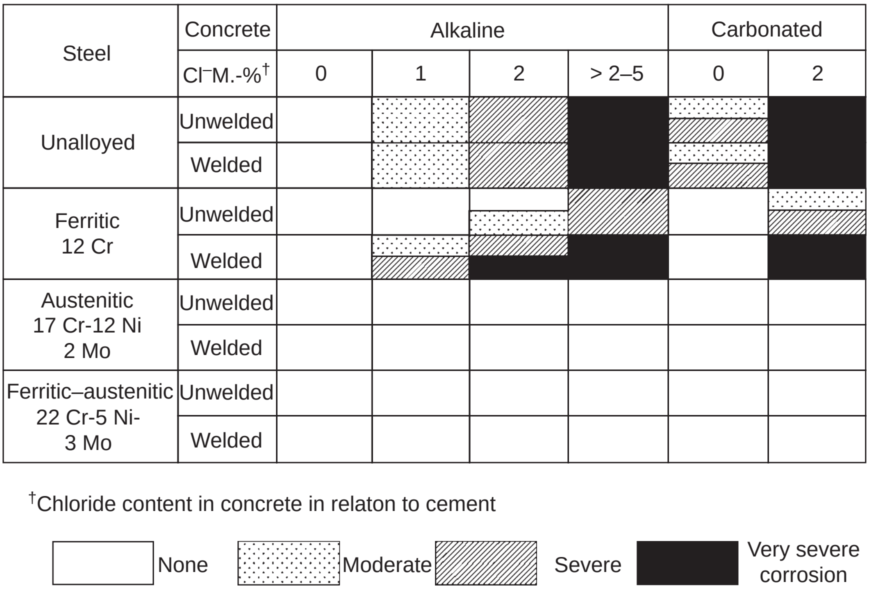
5.5 Macrocouple current density in a corroding bar of carbon steel in 3 % chloride-contaminated concrete when it was coupled (a) with a passive bar of unalloyed steel in chloride free concrete, (b) with bars of 1.4571 stainless steel in chloride free concrete, (c) with bars of 1.4571 stainless steel in 3 % chloride-contaminated concrete. Results are shown on stainless steel bars with and without the surface covered with oxide scale produced by heating at 700 °C in order to simulate a welding scale[14].

macrocouple is significantly lower than that of passive carbon steel. Thus, assuming the 'correct' use of the stainless steel, i.e. stainless steel is used in all situations where chloride ingress and subsequent corrosion might occur, the two metals can be coupled without problems.

The fact that stainless steel is a far less effective cathode in concrete than is carbon steel, makes stainless steel a useful reinforcement material for application in repair projects. When part of the corroded reinforcement, e.g. close to the concrete cover, is to be replaced, it could be advantageous to use stainless steel instead of carbon steel. In being a poor cathode, the stainless steel should minimise any possible problems that may occur in neighbouring corroding and passive areas after repair.

Field tests on stainless steel reinforcement

Concrete elements with cold deformed ribbed bars were exposed in the open air for up to 2.5 years[6]. The welded materials consisted of unalloyed and stainless steels 1.4003, 1.4462 and 1.4571. There was no treatment of the weld. Figure 5.6 summarises the results of this storage[6] and the results of the literature[9,10,12] and shows the corrosion degree based on pitting depth



Steel	Concrete	Alkaline				Carbonated	
	Cl⁻M.-%[†]	0	1	2	> 2–5	0	2
Unalloyed	Unwelded	□	░	▨	■	░ ▨	■
	Welded	□	░	▨	■	░ ▨	■
Ferritic 12 Cr	Unwelded	□	□	□ ░	▨	□	░ ▨
	Welded	□	░ ▨	▨ ■	■	□	■
Austenitic 17 Cr-12 Ni 2 Mo	Unwelded	□	□	□	□	□	□
	Welded	□	□	□	□	□	□
Ferritic–austenitic 22 Cr-5 Ni-3 Mo	Unwelded	□	□	□	□	□	□
	Welded	□	□	□	□	□	□

[†]Chloride content in concrete in relaton to cement

□ None ░ Moderate ▨ Severe ■ Very severe corrosion

5.6 Corrosion behaviour of steel in concrete (survey)[2].

and loss of weight. Results without and with weld are distinguished. As expected, mild steel bars corrode in carbonated- and/or in chloride-contaminated concrete. The strongest attack occurs in carbonated- plus chloride-contaminated concrete; cracking and spalling of the concrete specimens are common.

The unwelded low-chromium ferritic steel shows distinctly better behaviour than does unalloyed steel when embedded in alkaline concrete with low chloride levels. The critical chloride content for pitting corrosion is about 1.5 to 2.5 % depending on the state of the surface, type of cement (pH value of pore liquid) and concrete quality. However, at higher chloride content this steel suffers severe pitting attack, which is concentrated at a few points on the surface. The tendency to concrete cracking is distinctly lower than for corroding mild steel. In chloride-contaminated concrete the (unwelded) steel may suffer a stronger attack if carbonation had reached the steel surface.

For the welded steel within the weld line, chlorides produced locally display distinct pitting corrosion (see Fig. 5.7). The depth of pitting increases with increasing chloride content and is more pronounced in chloride-containing carbonated concrete. However, for the ferritic chromium steel the pitting at weld lines is deeper than for unalloyed steel, but the overall general corrosion (loss of weight) is significantly smaller. Further

5.7 Corrosion of deformed reinforcing bars in concrete (2 years; 2.5 M.-% Cl^-).

investigations[6] showed that the treatment of welded areas of specimens with a pickling paste improved the anti-corrosion behaviour.

All the higher alloyed stainless steels showed very high corrosion resistance in all the environments tested. No corrosion appeared with the austenitic steel CrNiMo 17-12-2 (1.4571) and the ferritic–austenitic steel CrNiMoN 22-5-3 (1.4462) whether in the unwelded or welded states. This was true for all conditions within the concrete: carbonated, alkaline and chloride-infiltrated, carbonated and chloride-infiltrated. As in the case of ferritic stainless steel, electrochemical studies[6,12] suggested that welding can affect the corrosion resistance of austenitic and ferritic–austenitic steels in chloride-bearing concrete and reduce the level of chloride contamination at which corrosion can take place. However, these studies also indicated that there was no corrosion of welded types 1.4571 and 1.4462 steel under practical conditions of strongly chloride-contaminated uncarbonated and carbonated concrete (chloride concentrations up to 5 %). Studies showed that the critical chloride concentration for unwelded rebars in chloride-containing concrete is more than ten times higher for austenitic and ferritic–austenitic stainless steel than for black steel[12].

The corrosion properties of austenitic and ferritic–austenitic Cr-Ni-Mo-steels were marginally better than for Cr-Ni-steels. Some results[9,12] suggested that, within this group of stainless steels, bars without molybdenum were sufficiently resistant and therefore suitable for application in chloride-contaminated concrete. Nevertheless, after the results of Sørensen et al.[12], welded bars without molybdenum do not seem to be sufficiently resistant and are unsuitable for application in the presence of more than 3 % chloride in concrete, related to the amount of cement.

In conclusion, one can say that ferritic stainless steel with at least 12 M.-% of chromium might be the best choice in moderately aggressive environments where higher resistance of more expensive austenitic stainless steels is not necessary. Austenitic stainless steel of type CrNiMo 17-12-2, even in the welded state, proved to give excellent performance in chloride-containing concrete, even at the highest chloride levels that are met in practical conditions. Austenitic stainless steel of type CrNi 18-10 may be satisfactory in many cases. Of comparable resistance are the ferritic–austenitic (duplex) steels. These materials may provide a suitable solution to the problem of concrete structures requiring rebars with high mechanical strength and good corrosion resistance. The use of stainless reinforcing bars based on the above recommendations can prevent steel corrosion in concrete structures that are needed for long service.

5.1.4 Application and practical experience

Stainless steel reinforcements have been used in concrete structures in the UK, Italy, Germany, Denmark, South Africa, Switzerland and Japan[2]. Standards for stainless steel reinforcement exist, for example, in the UK, Germany, Denmark and Italy. Typical applications of stainless steel reinforcement are structures that are exposed to very aggressive environments. An increasing amount of austenitic or ferritic–austenitic steel reinforcement is used in bridge engineering[3,18] where deicing salt can affect the structure. Furthermore, these steels are generally located at construction joints or at critical gaps between columns and deck. The use of higher quality steels will increase the reliability of multi-storey car park decks that are likely to be contaminated with deicing salts, concrete elements in thermal baths and piers at the sea-coast.

Ferritic stainless steel is used as reinforcement in pre-cast elements of normal-weight and lightweight concrete. Another typical application is in prefabricated wall elements with inner heat insulation where the reinforcement connects the outer and inner concrete walls. There are few applications of the long-term use of stainless steels as reinforcement in concrete; however, there have been numerous indications of their advantages[3].

A case of long-term application of stainless steel reinforcement (steel grades AISI 304 or respectively EN 1.4301) from the Mexican Gulf has been reported[19]. Due to the harsh environmental exposure of concrete piers in a hot and humid marine environment, it was decided to use stainless steel in selected areas. No significant corrosion was found 60 years after construction for the reinforcement with a cover larger than approximately 20 mm, despite the extremely high chloride content of up to 1.9 % Cl^- of dry concrete weight. For other piers at the same site reinforced with ordinary carbon steel serious chloride and/or carbonation-induced corrosion problems occurred.

5.1.5 Cost aspects

A responsible engineer will carry out a cost-benefit analysis and risk assessment of a construction including material cost, fabrication cost and maintenance cost. The experience shows corrosion protection even costing several times as much as normal reinforcement still to be a good and cheap solution when subsequent maintenance costs are taken into account, i.e. in special cases higher extra costs of the reinforcement may still offer the cheaper and better solution in the long term[3,18]. According to choice of protection system, extent of application (selected parts of the structure or the total project), the size of the bar, if the bars are straight or bent, the kind of structure and other factors, the price for corrosion protection may be about 1 to 15 % of the total costs. By contrast, conservative estimates of maintenance and replacement costs come to about 10 times the cost of additional corrosion protection of the reinforcement (prevention)[3,20], Klinghoffer et al.[21] reported that the 'intelligent' use of stainless steel, (i.e. a combination of stainless steel with traditional carbon steel) in locations exposed to very corrosive environments can be an extremely cost-effective option when considering different rehabilitation methods.

It is difficult to give specific advice as to when additional protection of the reinforcement is necessary and which kind is the best. Practical experience indicates that protective measures taken early, especially during design, strongly reduce the overall lifetime costs of a structure if there is a risk of corrosion[20]. The use of additional protective systems for the reinforcement seems to be necessary due to increasingly aggressive environments or the need for special construction applications.

An example of the different corrosion protection methods and their additional costs is discussed below[3]. A reinforced concrete wall (length 100 m, height 3 m and width 0.3 m) by the roadside exposed to splashing by traffic with chloride-containing water was constructed. It was decided to use those

Table 5.2 Additional corrosion protection of steel in concrete and its cost[3]

Corrosion protection	Price (Germany)		Cost of additional corrosion protection [€/m^2]	
			100% proportion protected	50% proportion protected[c]
Unalloyed steel		250 [€/t][d]	12[a]	
Galvanised steel	Galvanising	600 [€/t][d]	27	20
Epoxy-coated steel	Coating	440 [€/t][d]	23	18
Stainless steel 1.4571		2875 [€/t][d]	78	45
Nitrite-inhibitor	30 [l/m[c]] DCI S	1.1 [€/l]	17	
Cathodic protection	Design	4 [€/m[b]]		
	Material[b]	45 [€/m[b]]		
	Current	1 [€/m[b]]		
	Monitoring	70 [€/m[b]]	126	
	Σ	120 [€/m[b]]		
Coating of concrete (crack bridging)	Sand blasting	6 [€/m[b]]		
	Filling	14 [€/m[b]]		
	2 × sealing	15 [€/m[b]]	41	
	Σ	35 [€/m[b]]		

[a] Quantity of steel 0,025 [t/m^2] $\triangleq$ reinforcement ratio 1%, diameter: 12 mm.

[b] Titanium anode 30 [€/m^2], installation 5 [€/m^2], d.c. power supply/cable 10 [€/m^2].

[c] price of mixed reinforcement.

[d] cutting, bending, laying 250 [€/t].

structure: wall (length 100 m, height 3 m, width 0,3 m) beside a traffic road, treated with deicing salt.

corrosion protection methods summarised in Table 5.2 as an alternative to conventional carbon steel reinforcing bars. The table takes into account the initial costs of fabrication and installation of corrosion protection and regular corrosion induced maintenance costs in the case of cathodic prevention. The structural integrity is to be maintained for the full design life of 70 years.

The additional costs of corrosion protected reinforcement in some cases will vary with the bar diameter but it is very sensitive to the proportion of protected steel. Therefore, in some cases it is unlikely that the entire reinforcement would be made of corrosion-protected steel.

For the deicing salt-contaminated wall in Germany the additional corrosion protection costs between 2 and 10 times the price of steel without additional protection. The additional costs of various types of corrosion protection are shown in Table 5.3.

Table 5.3 Additional costs of different protection methods (for a selected structure see Table 5.2)

Type of coating	Costs
Unalloyed steel	100%
Galvanised steel	225%
Epoxy-coated steel	192%
Stainless steel	650%
Nitrite-inhibitor	142%
Cathodic protection	1050%
Concrete coating	342%

5.2 Stainless steel connections[22]

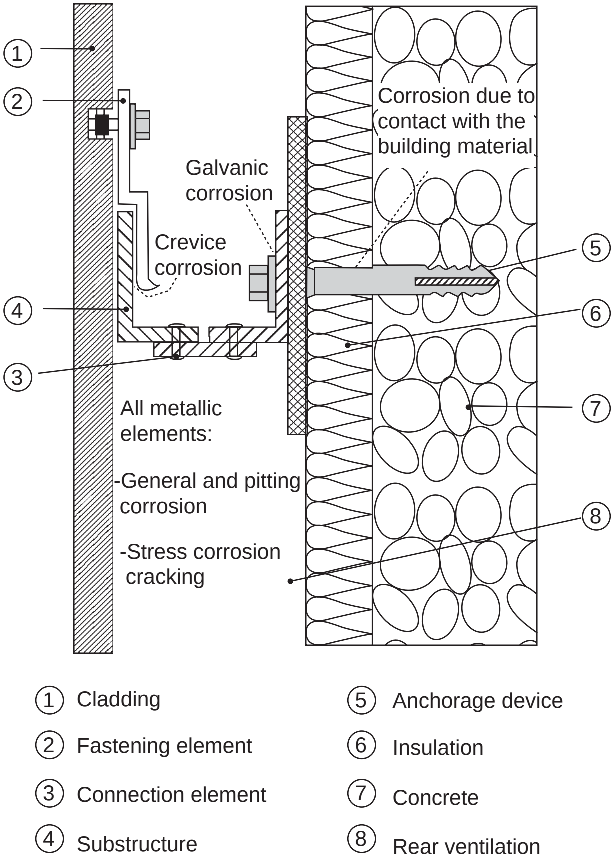
5.2.1 Introduction

During the last few decades pollution has increased in urban agglomerations, industrial areas and roadways. Because of this, the corrosion exposure of metallic structural elements is growing. Mechanical connection elements between steel and concrete, e.g. in claddings for external walls that are ventilated at the rear and comply with DIN 18516[23], in suspended ceilings in special climates (humid premises, indoor swimming-pools) or in flat roofs are also affected. Due to corrosion, connection elements can undergo an impairment of their functionality as well as making a security risk for the whole construction. In the past, steel fastenings that are galvanised and plastic coated have been particularly affected in the exterior. Corrosion could especially be explained by high chloride pollution of the atmosphere and the building materials and/or contact with moist building materials during failures[22]. At contact with moist, neutrally-reacting building materials (e.g. heat insulation, wood), corrosion-protective films cannot develop and corrosion-promoting aeration cells become effective[4]. Additional serious corrosion damages have occurred in indoor swimming-pools in connection elements that consisted of stainless steel[4,24]. The use of unsuitable steel grades in an aggressive atmosphere was responsible for these damages.

Because of the correlation mentioned above, high-quality stainless steels have been tested regarding applications in structurally critical climates[25,26,27] and have also been increasingly used for steel connections, fastenings, substructures, hangers and anchorage devices in structural elements out of doors[28]. The adequate steel grades are regulated with special approval (see Section 5.2.4) depending on corrosion exposure and installation conditions.

5.2.2 Corrosion problems in claddings for external walls with rear ventilation

Under critical exposure conditions various corrosion processes are possible in mechanical connection elements as well as in adjacent metallic structural elements. This is illustrated in Fig. 5.8 which is an example of a ventilated curtain wall. Table 5.4 quotes the structural elements, i.e. the building materials of the cladding for external walls as well as fastening elements, connection elements and anchorage devices that have to be put in. It can be ensured that, with constructions such as external walls as well as a choice of suitable building materials, damaging influences in the case of attack by water and especially aqueous, acidic and/or chloride-enriched media do not lead to a corrosion impairment. In general, stainless steel can be used for all metallic structural elements and it can also be used in contact with different structural metals.



5.8 Cladding for external walls with rear ventilation[22].

Table 5.4 Structural elements in an external ventilated curtain wall[22]

Mark	Structural element	Type of construction	Material
1	Cladding	Moulded metal sheet, plate	Ceramics, natural stone, fibre cement, high pressure laminated plate, aluminium alloy, copper, titan zinc, galvanised and/or coated steel, stainless steel
2	Fastening element	Screw, rivet, cramp, hook	Aluminium alloy, copper alloy, stainless steel
3	Connection element	Screw, rivet	
4	Substructure	Profile (load-bearing rail)	Aluminium alloy, copper alloy, galvanised and/or coated steel, stainless steel, wood
5	Anchorage device	Post-installed fastener, anchor rail, concrete screw	Stainless steel, plastic sleeve plus galvanised screw
6	Insulation	Mat	Mineral fibre, glass fibre, styrofoam

5.2.3 Exposure conditions for connection elements[4,29]

Atmospheric corrosion depends on humidity and temperature as well as on the concentration of gaseous and/or solid contamination in the air. Therefore, corrosion exposure of structural elements in the open air is distinguished by:

- Climatic zones (dry, temperate, warm, or humid climate).
- The type of atmosphere that is characterised through local environmental conditions: an inland atmosphere, as a rule, is not very aggressive. Urban atmospheres and especially industrial atmospheres can be badly polluted with dirt, sulphur-dioxide or deicing salt. Sea atmospheres are, depending on the distance to the shore, polluted with variable contents of chloride aerosols.
- Microclimates at the interface between the structural element and environment; this is of the greatest influence for the expected corrosion exposure. It is specified by the type of atmosphere, constructive influences (heat-leaks, crevices) and the position of the structural element in regard to its environment. A microclimate is influenced by humidity, temperature, dew-point, duration of local moistening and air flow as well as polluting agents.

Special applications exist and are described below.

5.2.3.1 Interior work

The external surfaces of structural elements and connectors inside buildings do not usually get into contact with aqueous corrosion media. A corrosive exposure only takes place if water, moistness of structural elements or other polluting agents cause problems because of failures.

5.2.3.2 Road tunnels

In road tunnels, fastening elements of steel are exposed to an enhanced relative humidity, a high portion of dust, soot, car tyre abrasion and chloride salts from deicing salts and acid gas such as SO_2, HCl and NO_x (as a consequence of diesel vehicles). Because of the lack of rain, a concentration of polluting agents occurs. Since in addition, the tunnel wall and the metallic components that are fastened to it usually have lower temperatures than the surrounding air, suitable conditions are given for the condensation of water. Under these conditions a water film that is acidic and rich in chloride ions forms on the metallic components and, because of dirt deposits the basic requirements for crevice corrosion are also met. In particularly adverse cases, the corrosion conditions are comparable to those in indoor swimming-pools.

5.2.3.3 Indoor swimming-pools

In the swimming-pool atmosphere very thin electrolyte films are generated because of the water vapour content in the air and, depending on aeration and structural conditions, condensation water develops after the short-fall of the dew-point. Further, salts and dusts, that, among others, contain $MgCl_2$, $CaCl_2$ and especially NaCl, are deposited. Because of their hygroscopic character these salts generate saturated salt solutions in the typical relative atmospheric humidity of 'dry' interiors. A further characteristic of the corrosion power of the atmosphere in indoor swimming-pools results from the disinfection treatment of the bath-water. The chlorinated gas process is usually applied. Chlorine, that is in the air above the swimming-pool can, in reaction with water, form hydrochloric acid (HCl) and hypochlorous acid (HOCl) in surface films that are rich in neutral salts, according to the reaction

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad [5.1]$$

It is the hypochlorous acid that acts as a disinfectant, because of its strong oxidation effect. In water it disintegrates into hydrochloric acid and oxygen according to the equation:

$$2HOCl \rightarrow 2HCl + O_2 \qquad [5.2]$$

In this way, an acidic and saline electrolyte with a high concentration of chloride ions develops on the surface of the structural element. Polluting agents accumulate on surfaces of structural elements that are not cleaned and washed by water.

5.2.3.4 Characteristics of connection elements

Connection elements are often inaccessible. They are, for instance, behind walls or above covered ceilings, not within reach for inspections and maintenance. In addition, connection elements can, at least, be partially in contact with mineral building materials (concrete), insulation or wood. Then, with regard to corrosion exposure, the conditions mentioned above, especially the microclimate, are of importance for those zones that come into contact with air. The corrosive exposure, that for instance has to be expected in claddings for external walls that are ventilated at the rear according to DIN 18516, Part 1[23], results from atmospheric influences (relative atmospheric humidity, access of acidic gases and chloride aerosols) in close connection with structural parameters of the wall construction and chemical influences from (moist) building materials. In walls and façades that meet the technical standards concerning humidity (proof of protection against interior condensation and absence of dew-water in the area that is ventilated at the rear[30]) or comply with the standards mentioned in DIN 18516 Part 1[23] (incoming moisture has to be eliminated because of ventilation at the rear), it can be assumed where there is flawless protection against outdoor weathering (water-proof joints preventing any ingress of rain from outside) that in normal cases the corrosion exposure is less than it is in outdoor weathering. Formation of condensate only occurs for a short time, e.g. as a result of the heat-leak effect of fastening components, although corroding polluting agents, especially chlorides (from some building materials or from aerosols) can concentrate, because they cannot be washed off by the rain.

Regarding those connection elements that come in contact with building materials, whether they contain in their pores and inner cavities the free water that is necessary for corrosion to take place is important[4,31]. Furthermore, in the case of stainless steel, conditions that inhibit or destroy passivity have to exist. In all cases of corrosion, a complicating factor is caused by water dissolving ingredients from the building materials that corrode steel or allowing the transport of polluting agents from the environment to the building material.

The corroding influence of materials on stainless steels can only be expected if these materials contain a sufficient concentration of chloride ions and/or acids in addition to water. Chlorides can only get into normal concrete in high concentration if there is a direct impact with sea water or water containing deicing salts[4]. Normally, such exposure of connecting elements and building materials with chloride-containing water does not happen in practice. Acetic acid that can also attack stainless steel can be released from moist wood depending on the type of wood, because of hydrolysis at increased temperatures[4]. In certain cases, chemicals for wood protection can also contain chlorides.

Moist insulation materials are not only conducive to general corrosion. Because of their electrolytic conductivity they can promote the formation of substances between structural elements in the insulation (e.g. of galvanised or non-galvanised, unalloyed steel) and more important components. Examples of so-called foreign cathodes are steel in concrete, copper materials and stainless steels if they are conductively connected to the steel elements in the insulation that are effective as anodes. Insulation should be free of corrosion-promoting components that could be dissolved in any water present.

5.2.4 Definition of the grades of resistance according to the approval of the German building supervisory board

Reduction of the cross-section, pitting corrosion and stress corrosion cracking are important for the technical corrosion resistivity of connection elements. Table 5.5 gives a general view of the admitted steels as well as the classification according to the grades of resistance[32]. The quality of the steels increases depending on the rising grade of resistance. This specific standard for stainless steels concerning alloy results from the particular corrosion exposures (e.g. attack of chloride ions or acid) and such resistivity as may be required against heavy corrosion attack.

For metallic connecting elements and adjacent structural elements, ferritic, austenitic, ferritic–austenitic and martensitic steels can be used, but ferritic and martensitic steels are only exceptionally used for screws and the use of austenites predominates. They are used in different strength levels from a solution-annealed to a cold deformed state. In the usual case, connecting agents in structural elements in the outdoors should be those of the third grade of resistance. In many cases, e.g. behind walls, connecting agents are inaccessible to inspection and maintenance and a moderate exposure with chloride and sulphur dioxide from industry, traffic and sea atmosphere is often inevitable. If there is a concentration of polluting agents the use of steels of the fourth grade of resistance is necessary.

Because of the possibility of failure, special regulations have been adopted for structural elements in indoor swimming-pool constructions. For fastening elements that are not cleaned regularly, such as hangers for

Table 5.5 Classification of the steel grades for structural elements and connection elements according to strength levels and grades of resistance against corrosion[32]

Material	Symbol	Strength level	Grade of resistance	Corrosion exposure, typical applications
1.4003	X2Cr 11	S235, S275 S460	I	Indoor exposure
1.4016	X6Cr 17	S235		
1.4318	X2CrNiN 18-7	S355, S460	II	Accessible constructions without appreciable contents of chloride and sulphur dioxide
1.4567	X3CrNiCu 18-9	S235, S275, S355, S460		
1.4301	X5CrNi 18-10	S235, S275, S355, S460		
1.4541	X6CrNiTi 18-10	S235, S275, S355, S460		
1.4401	X5CrNiMo 17-12-2	S235, S275, S355, S460	III	Non-accessible constructions with moderate chloride and sulphur dioxide exposure
1.4404	X2CrNiMo 17-13-2	S235, S275, S355, S460, S690		
1.4571	X6CrNiMoTi 17-12-2	S235, S275, S355, S460, S690		
1.4439	X2CrNiMoN 17-13-5	S275		
1.4462	X2CrNiMoN 22-5-3	S460, S690	IV	Constructions with high corrosion exposure by chloride and sulphur dioxide (also in cases of concentration of polluting agents, e.g. elements in sea water and road tunnels)
1.4539	X1NiCrMoCuN 25-20-5	S235, S275, S355		
1.4529	X1NiCrMoCuN 25-20-7	S275, S355, S460, S690		
1.4565	X3CrNiMnMoNbN 23-17-5-3	S460		
1.4547	X1CrNiMoCuN 20-18-7	S275, S355		

ceilings and for anchorage devices the regulations given in Table 5.6 have been adopted with particularly high standards for the steels. Today, structural elements and connecting agents, e.g. in ventilated curtain walls, are mainly made of the materials 1.4301 (A2) and 1.4401 (A4) and therefore only comply with the second or third grade of resistance. Steels of higher

Table 5.6 Structural elements in typical indoor swimming-pool atmosphere where there is no regular cleaning[32]

Domestic water ($Cl^- \leq 250\,mg/l$)	Chloride enriched water (e.g. saline water)
1.4539 (X1NiCrMoCu 25-20-5)	1.4565 (X2CrNiMnMoNbN 23-17-5-3) 1.4529 (X1NiCrMoCuN 25-20-7) 1.4547 (X1CrNiMoCuN 20-18-7)

resistance (e.g. 1.4529) are used for anchorage devices (post-installed fasteners) that have to comply with much higher demands.

The development of stainless steels for the field of construction as well as for mechanical connectors has been very much influenced by damage in indoor swimming-pools due to stress corrosion cracking over the last ten years. In 1985 there was a serious crash of a reinforced concrete roof that was hung on hangers of stainless steel 1.4301. Since this accident, examinations of important construction elements have been conducted in many other indoor swimming-pools in Switzerland, Germany, England and the US and additional examples of stress corrosion cracking were found[4,24,29]. The materials containing molybdenum (e.g. 1.4401) proved to be more resistant, but stress corrosion cracking was also detected there. Analysis of the damages and results of the research[25,26,27] finally led to the conclusion that only those higher alloyed materials listed in Table 5.6 are sufficiently secure under these critical environmental conditions.

5.2.5 Outlook

Present and future efforts are aimed at the creation of self-drilling screws for steel substrates (e.g. for the connection of coverings and substructures) and concrete screws made of very high strength martensitic steels. Self-drilling screws drill their pilot hole in the steel themselves during the mounting and concrete screws are especially made to be anchored in concrete, and are screwed into a prepared hole. In both cases cold deformed austenitic steels are used at present. Since they cannot yet be screwed into hard substrates (steel, concrete) in the required way, a tip of screw of a hardenable unalloyed steel is butt welded, for example. Efforts are being made to produce completely the above-mentioned fastenings, i.e. anchors from a martensitic steel of high hardness; but the corrosion resistivity of such materials is limited. Martensitic steels proved to be susceptible to crevice corrosion and stress corrosion cracking, especially in the case of an attack of chlorine electrolytes[7].

5.3 Sources of further information and advice

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6

Surface treatments and coatings for corrosion protection

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6.1 Introduction

A package of standards on the protection and repair of reinforced concrete is currently being drafted by CEN TC 104. The central standard in this package is EN 1504, which comprises 10 parts – see Table 6.1. Part 1 describes the general scope of application and provides definitions. Parts 2 to 7 concern the materials that are used for the protection and repair of concrete components. Part 8 specifies the quality assurance for manufacture of the products concerned, while Part 10 specifies the requirements for execution including quality assurance. The protection and repair principles that are based on sciences of nature, and the methods to implement these principles, are described in Part 9. The following descriptions are based on the stipulations contained in standards series EN 1504.

6.2 Principles and methods for protecting reinforcement against corrosion

6.2.1 General

Reinforcement corrosion can be caused by:

- Physical loss of the concrete cover.
- Loss of alkalinity in the concrete cover as a result of carbonation.
- Contamination of the concrete by corrosion-promoting substances (usually chlorides).
- Electric stray currents that are introduced into the reinforcement from adjoining electrical installations.

The most important step in planning a repair project is the selection of suitable repair principles, by means of which corrosion of the reinforcement can be prevented, slowed down or stopped under the given parameters. The preliminary selection of principles must be carried out on the basis of an

Table 6.1 Parts of EN 1504

Part number	Part title
1	General scope and definitions
2*	Surface protection systems (concrete coatings)
3*	Structural and non-structural repair (mortars and concretes)
4*	Structural bonding (steel plates and fibre reinforced polymers)
5*	Concrete injection
6*	Grouting to anchor reinforcement or to fill external voids
7*	Reinforcement corrosion protection (steel coating)
8*	Quality control and evaluation of conformity
9**	General principles for the use of products and systems
10*	Site application of products and systems and quality control of the works

* Draft.
** Prestandard.

expert appraisal of the state of the building structure and should ideally cover two or three alternative strategies. The possible repair methods should be compiled for all the principles that are applicable in the case concerned. The final decision in favour of a repair principle and a repair method is reached with due regard to the available materials and, where applicable, the company that is to carry out the repair work.

The principles and methods that can be applied to prevent or slow down reinforcement corrosion are presented in Table 6.2 and the methods discussed in this chapter indicated. In accordance with EN 1504-9, Appendix B, it is permissible to combine several protection and repair methods, where it is of crucial importance to take possible interactions into account. Such interactions may be desired or undesired. Due consideration must also be accorded to any possible negative effects on reinforcement corrosion of a method which is intended to protect or repair the concrete, e.g. by increasing the concrete's moisture or temperature level. Examples of undesired effects are presented in Table 6.3.

6.2.2 Principle 1 (PI) protection against ingress

This section discusses the methods employing surface protection systems (1.1 and 1.2) and crack-filling materials (1.4), see Table 6.2.

6.2.2.1 Methods 1.1 and 1.2 – impregnation and surface coating

Methods 1.1 and 1.2 involve the use of impregnating agents and coatings and are discussed further in Section 6.7.

Table 6.2 Principles and methods of protection and repair

Principle			Methods	
No	Short cut	Definition	No	Definition
1 (PI)	Protection against ingress	Reducing or preventing the ingress of adverse agents (e.g. water, chlorides)	1.1*	Impregnation (blocking of the pore system)
			1.2*	Surface coating
			1.3	Locally bandaged cracks
			1.4*	Filling cracks
			1.5	Transferring cracks into joints
			1.6	Erecting external panels
			1.7	Applying membranes
7 (RP)	Preserving or restoring passivity	Creating chemical conditions in which the surface of the reinforcement is maintained in or returned to a passive condition	7.1*	Increasing cover to reinforcement with additional cementitious mortar or concrete
			7.2*	Replacing contaminated or carbonated concrete
			7.3	Electrochemical realkalisation of carbonated concrete
			7.4*	Realkalisation of carbonated concrete by diffusion
			7.5	Electrochemical chloride extraction
8 (IR)	Increasing resistivity	Increasing the electrical resistivity of the concrete	8.1*	Limiting moisture content by hydrophobic impregnation
			8.2*	Limiting moisture content by coating or sheltering
9 (CC)	Cathodic control	Creating conditions in which potentially cathodic areas of reinforcement are unable to drive an anodic reaction	9.1	Limiting oxygen content (at the cathode) by saturation or surface coating
10 (CP)	Cathodic protection		10.1	Applying electrical potential
11 (CA)	Control of anodic areas	Creating conditions in which potentially anodic areas of reinforcement are unable to take part in the corrosion reaction	11.1*	Painting reinforcement with coatings containing active pigments
			11.2*	Painting reinforcement with barrier coatings
			11.3	Applying inhibitors in the concrete

* discussed in this chapter.

Table 6.3 Examples of undesirable consequences of protection and repair methods

Method	Undesirable potential consequence
Reduction of concrete humidity	Increase of carbonation progress
Coating of concrete surface	Adhesion failures and lower frost resistance through water that penetrates into uncoated areas and cannot exit
Prestressing after placing of concrete	Stresses out of control in the building component
Electrochemical methods	Embrittlement of sensible prestressing steel, intensifying of alkaline–aggregate reaction, lowering of frost resistance through higher concrete humidity
Interruption of oxygen input to cathodic areas by coating	Extensive potential reversal through uncompleted coating

6.2.2.2 Method 1.4 – filling cracks

Cracks whose width is within the limits stipulated in EN 1992-1-1 and which are controlled by the reinforcement are not infrequent in reinforced concrete and do not require further consideration. Cracks outside this range may result from various causes, e.g. induced hygric stress (shrinkage), thermal stress or overloading.

Firstly, a competent planner must assess the influence of the cracks on the load-bearing capacity, serviceability and durability of the concrete component. This assessment is based on a description of the cracks by reference to key characteristics. Methods are presented in *Deutscher Ausschuß für Stahlbeton*, Part 2, Table 6.1 (see Section 6.9). In every instance, the causes of the cracking and the effects of harmful substances penetrating into or seeping through the component must be established. Information must also be provided regarding the necessity of filling the cracks, the objective of the measure, movement of the crack edges and, where appropriate, on the risk of new cracks arising.

Crack filling pursues one or more objectives:

(a) To inhibit or prevent the penetration of corrosion-promoting substances into the concrete.
(b) To seal a permeable component.
(c) To seal the crack while maintaining limited elasticity.
(d) To connect both sides of the crack allowing a load transfer.

The main focus for the purposes of preventing, slowing down or stopping reinforcement corrosion is on objective (a). This objective is attainable with any of the substances specified in Section 6.5.1, according to the given parameters. Elastic and fixed joints are generally mutually exclusive. As a rule, cracks smaller than 0.3 mm can only be sealed durably without additional concrete coating if there are no changes to the width of the crack. Fixing a crack is only viable when the tensile strength of the concrete is not exceeded in the area surrounding the crack in the further course of use of the component. The competent designer is responsible for assessing this aspect. The further growth of cracks that have occurred as a result of reinforcement corrosion cannot be prevented by filling alone. In order to reduce or stop reinforcement corrosion, repair principles 7–11 must be observed.

6.2.3 Principle 7 (RP) preserving or restoring passivity

6.2.3.1 General

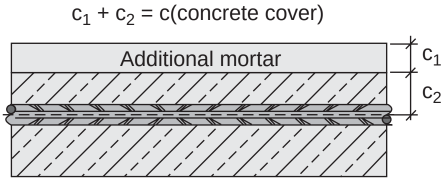
Carbonation of the concrete and the attendant drop in the pH value of its interstitial solution results in destruction of the passive layer on the steel surface. The methods stated in accordance with Principle 7 are intended to prevent, slow down or stop this destruction. All the methods that restore passivity are only effective down to a limited depth. There is a danger of harmful substances migrating into the component from outside or from concrete in the vicinity that contains harmful substances.

6.2.3.2 Method 7.1 – increasing cover to the reinforcement

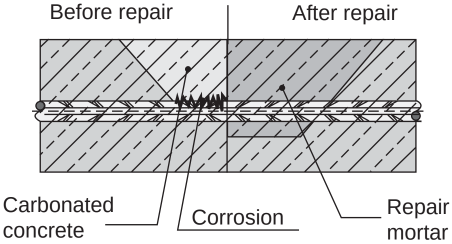
Method 7.1 involves increasing the thickness of the concrete cover by using additional cementitious mortar or concrete. This is alkaline and maintains the alkaline environment in the area of the reinforcement. It thereby preservers the passive layer on the steel surface and/or prevents corrosion of the reinforcement during the component's service life. The application of method 7.1 is presented in diagram form in Fig. 6.1.

6.2.3.3. Method 7.2 – replacing contaminated or carbonated concrete

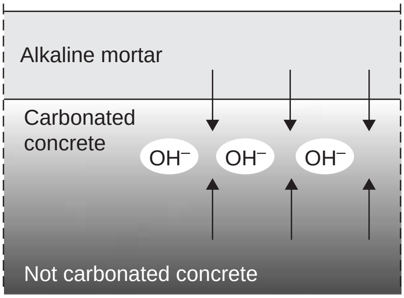
Method 7.2 can be applied both when the reinforcement surface has not yet been depassivated and when it already reveals signs of corrosion. Here the reinforcement must not be coated as the pH value of the mortar will otherwise remain ineffective. If the concrete is removed in highly localised areas only, it may be expedient to protect the repair mortar or concrete and the adjoining old concrete from penetration by harmful substances by means of Methods 1.1, 1.2, 1.6 or 1.7. The application of Method 7.2 is presented in diagram form in Fig. 6.2.



6.1 Method 7.1, increasing cover to reinforcement with additional cementitious mortar or concrete.



6.2 Method 7.2, replacing contaminated or carbonated concrete.



6.3 Method 7.4, realkalisation of carbonated concrete by diffusion.

6.2.3.4 Method 7.4 – realkalisation of carbonated concrete by diffusion

The aim of Method 7.4 is to form a new passive layer on the reinforcement surface (repassivation). This can be achieved by applying a cement-bound mortar or concrete (referred to below simply as mortar), resulting in the restoration of a high pH value on the steel surface. To this end, the repair mortar must possess an adequate level of alkalinity or adequate carbonation resistance. The method is employed both in localised areas and over large surfaces. The application of Method 7.4 is presented in diagram form in Fig. 6.3.

Only loose concrete requires removal. Where necessary, however, sufficient old concrete is also removed in the area next to the reinforcing rods, to enable the repair mortar to be introduced without any voids (10 or 15 mm when a rod diameter of ≥20 mm applies). If the mean carbonation depth is more than 20 mm behind the outermost reinforcement layer, the old concrete is removed up to the middle of the outer reinforcement layer, in order to enable adequate realkalisation. The exposed reinforcement surface must then be treated such as to attain a surface preparation level of at least Sa 2 in accordance with ISO 12944-4.

As a rule, the carbonation resistance of a component is improved by coating its entire surface with a surface protection system (see Section 6.7). The effectiveness and limited durability of this system must be recognised in the maintenance plan. In the case of local reprofiling, the application of a surface protection system can only be waived if, after repair, the thickness of the concrete covering also exceeds the carbonation depth outside of the reprofiled areas without a surface protection system at the end of the service life. Regardless of this, the method should only be employed if the thickness of the concrete covering is at least 10 mm after the repair work. In other cases, Principles 8 or 11 should be applied, for example.

6.2.4 Principle 8 (IR) increasing resistivity

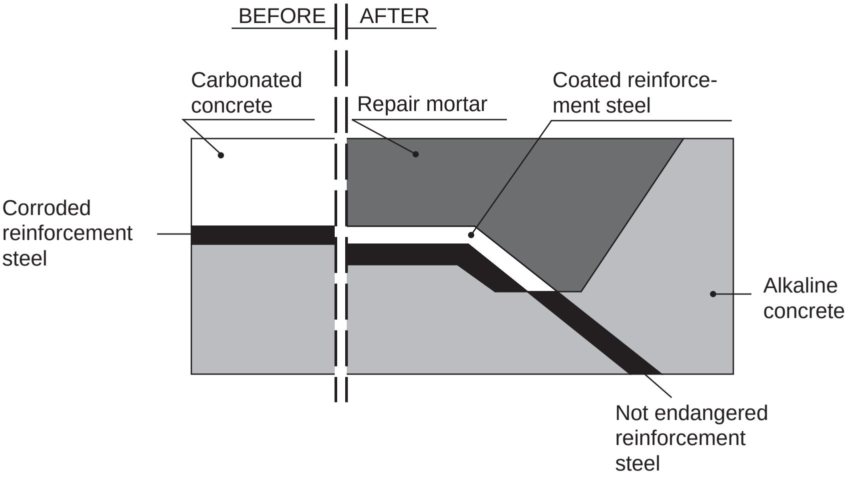
Principle 8 is based on a lowering of the concrete's water content, which reduces electrolytic conductance and thus the potential ionic current to such an extent as to slow the rate of corrosion to practically negligible values.

6.2.4.1 Methods 8.1 and 8.2 – hydrophobic impregnation and coating or sheltering

These methods involve limiting moisture content by surface treatments, coatings or sheltering. They can take the form of hydrophobic impregnation (EN 1502, 8.1) or coating (EN 1502, 8.2). These processes can be achieved by means of appropriate surface protection systems (see Section 6.7.2 and 6.7.4) or coverings (e.g. metal) that are largely able to prevent water from penetrating into the component. Water vapour must also be prevented from penetrating into the component from the inside of the component or as ground damp.

6.2.5 Principle 11 (CA) control of anodic areas

Principle 11 is based on preventing the anodic dissolution of iron by means of a suitable coating on the steel surface. It is applied when the requirements pertaining to repair Principles 7 and 8 are not possible. This is the case, in particular, when the thickness of the concrete cover remains below



6.4 Principle 11 (CA) control of anodic areas.

10 mm after repair, rising damp applies or the rear side of the component is subject to damp. The influence on the bond with the reinforcement must be taken into account. The application of Principle 11 is presented in diagram form in Fig. 6.4.

6.2.5.1 Method 11.1 – painting reinforcement with coatings containing active pigments

The mode of functioning of these coatings is based on the active pigments acting as anodic inhibitors or local sacrificial anodes. Inhibitors prevent the formation of anodic regions in the reinforcement. As a result of coating with an electrical conductor that has a lower electrode potential than steel, the cations of the coating metal dissolve in corrosive conditions before the steel. The ions of the coating metal are additionally attracted to local free (negatively charged) areas of the steel surface, as a result of which they regenerate the protective layer.

6.2.5.2 Method 11.2 – painting reinforcement with barrier coatings

The coating on the steel should insulate it electrically. This is intended to prevent the migration of metal cations out of the steel and the discharge of incoming anions. This method can only be effective if the steel is free of any contamination and if it is covered completely by the coating in the area concerned. The coating must be free of flaws and defects, including those in the micro-range. The old concrete must be removed in the areas to be repaired (e.g. carbonated areas) around the reinforcing rods. To enable the repair mortar to be introduced without any voids and the steel surface to be prepared and coated without any flaws, at least 10 mm of concrete should be removed from around the rod. The exposed steel surface is then derusted by blasting with a dry or moist blasting agent so as to achieve a surface preparation level of Sa 2 1/2 in accordance with EN ISO 12944-4. This also applies to crossing areas of concrete rods and the rear sides of the steel surfaces. If it is not possible to remove the carbonated or contaminated old concrete on the scale described above or if the resistance of the concrete to harmful substances requires additional improvement, the method can be combined with Method 8.1 or 8.2.

6.3 Substrate preparation

6.3.1 General

The lasting effectiveness of a repair measure is contingent on careful preparation of the substrate. The aim of every substrate treatment method is to achieve the best possible bonding between the substrate (concrete, mortar or steel) and the repair material that is to be applied.

Treatment of the substrate pursues different objectives, according to the specifics of the given situation:

- The removal of coatings and films (e.g. paint, curing membranes, soiling).
- The removal of thin, brittle films (e.g. cement slurry).
- The removal of concrete and mortar.
- Derusting of the reinforcement.
- Cleaning (e.g. of steel).

All loose parts of the substrate must always be removed. In addition, it may also be necessary to remove solid matter such as old concrete if its chloride content is too high or if the steel must be exposed, for example. The substrate is also treated in order to increase its roughness and thus to create a large surface area, thereby enhancing bonding of the subsequent layer. In many cases it is expedient to close cracks prior to treating the substrate.

6.3.2 Substrate treatment methods

Various methods of substrate treatment are available. An overview of the methods to prepare the concrete substrate is given in *Deutscher Ausschuß für Stahlbeton*, Part 2, Table 2.5 (see Section 6.9). The table also specifies the appurtenant objectives, areas of application, parameters and required reworking.

6.3.2.1 Chiselling, milling and flame-cleaning

When chiselling, it is important to ensure that no damage occurs to the steel, and to the prestressing steel in particular. Even the smallest notches on the surface of heat-treated prestressing steel may result in its sudden failure.

A broad spectrum of equipment is available for milling. The range extends from small, manual devices to large-scale equipment, including self-propelled devices. The risk of damaging the remaining concrete zones close to the surface increases when heavy-duty milling machines are used.

Flame-cleaning is carried out by heating the near-surface concrete zone with a gas flame heated to around 3000 °C. The sudden expansion of quartz at temperatures above 600 °C and the pressure resulting from evaporating interstitial water causes layers of concrete near the surface to break off. The removal depth can be set between 1 and 4 mm via the feed rate of the burner (1 m/min at least). This method may only be applied when an adequately thick covering of concrete is available, so as to ensure that the reinforcing steel is not damaged. The heat-treated surface must always undergo subsequent treatment by means of a mechanical method (blasting, milling, brushing), in order to remove the concrete zones with structural flaws down to the substrate which is capable of bearing a subsequent layer.

6.3.2.2 Blasting with solid abrasives

Blasting with solid abrasives is one of the most commonly used and most versatile methods. Loosely held matter is detached by the high-speed impact of the blasting agent on the surface. The most commonly employed abrasives are aluminium oxide, silicon carbide and copper melting chamber slag. Dry quartz sand harbours the risk of silicosis for personnel and should therefore only be used in combination with good extraction facilities and appropriate dust protection for the personnel (protective helmet with fresh air supply at least, or fully protective suit).

Shot-peening involves blasting steel pellets of around 1.5 mm in diameter onto the surface by means of compressed air. The detached particles are extracted together with the steel pellets and separated from the latter in the shot-peening device. The pellets that are recovered in this way are subsequently recycled. In order to reduce the incidence of dust, there is a growing tendency towards the use of wet-blasting methods where water is added to the blasting material in the blasting nozzle.

6.3.2.3 High-pressure water blasting

High-pressure water blasting has acquired exceptional importance in recent years on account of the following advantages:

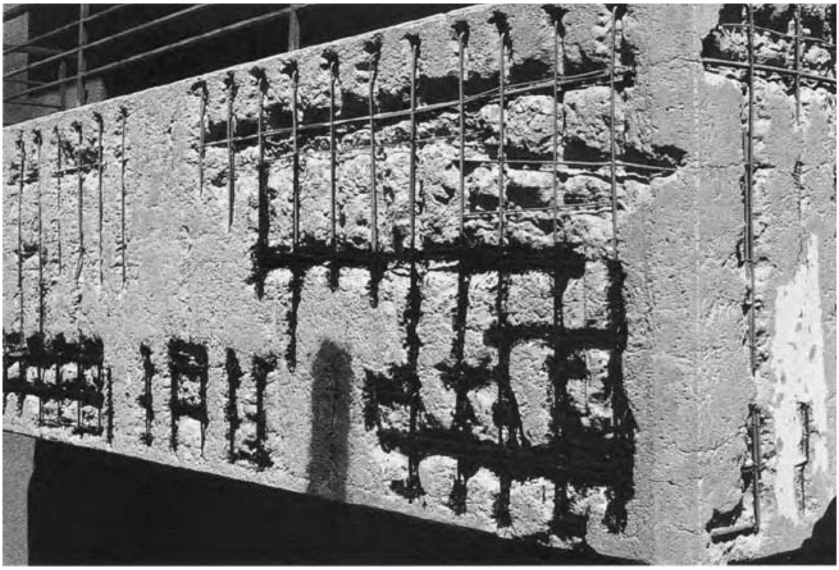
- High material removal rates.
- Large removal depths.
- Material removal behind the reinforcement also possible.
- No damage to the load-bearing substrate.
- No damage to the reinforcement.
- No subsequent treatment necessary, except for cleaning.
- Vibration-free mode of operation.
- Low noise emissions.

The term ‘high pressure’ is used when pressures of 60 to 120 MPa (600–1200 bar) apply, while ‘ultra-high pressure’ refers to the range from 120 to 270 MPa. High-pressure water blasting, at a water discharge rate of up to 250 litres per minute, is suitable for removing concrete over large areas and to great depths. Ultra-high pressure levels and low water flow rates (<40 l/min) are suitable for removing highly stable layers and for cutting purposes. Apart from pressure and water volume, other factors influencing the material removal depths and surface area removal rates are the nozzle design and movement, blasting distance and angle and the stability of the concrete substrate. When high pressure and large volumes of water are employed, the nozzles are usually operated automatically, partly on account of the high recoil forces; when large, horizontal surfaces are involved, these may be installed on a self-propelling device. When subsequently applying a surface protection system or carrying out reprofiling, it may be necessary to wait for the concrete substrate to dry before proceeding to this subsequent stage.

6.3.3 Derusting the reinforcement

Derusting of the reinforcement is subject to varying requirements according to the selected repair method (see Sections 6.2.3 and 6.2.5). Only mechanical methods should be used for this purpose and they must be carried out in accordance with EN ISO 12944-4.

Surface preparation level Sa 2 1/2 which is required for repair Principle 11.2 is attained by blasting with a solid abrasive. Surface preparation level Sa 2 is sufficient for steel surfaces that are not to be coated with a corrosion-proofing agent in connection with repair Principles 7 and 8, i.e. only loose corrosion products have to be removed. Blasting methods employing dry and wet blasting agents and high-pressure water are suitable for this purpose. Figure 6.5 shows a concrete component on which virtually the entire outer reinforcement layer has been exposed and derusted by means of blasting.



6.5 Reinforcing exposed by blasting.

6.4 General information on quality assurance and the use of materials

The essential suitability of all materials and material systems must be verified in a test. The requirements and test methods are specified in the parts of EN 1504 relating to the materials (Parts 2 to 7). The quality of the products is monitored by factory production control (see EN 1504-2 to -8) and the quality assurance procedure for the works on site specified in EN 1504-10.

The manufacturer's instructions for use must be observed when using repair materials. Such instructions contain information on:

- Composition and mode of procedure for mixing.
- Permissible parameters regarding temperature and moisture content of component, substance/material and air.
- Substrate treatment.
- Equipment and procedures.
- Workability times.
- Layer thicknesses.
- Required amounts of substances and materials.
- Waiting times.
- Treatment/curing.
- Key data on the materials.

- Safety, ecology, occupational safety.
- Disposal.

6.5 Filling cracks and cavities in concrete

6.5.1 Crack-filling materials

Epoxy resins (EP), polyurethane resins (PUR), cement paste (CP) and cement paste suspensions (CS) are employed as crack-filling materials. In recent years acrylic gels have also been used under special circumstances.

6.5.1.1 Epoxy resins

Epoxy resins are used for injecting into cracks to produce fixed joints. They consist of 2 components, a resin and a hardener, are solvent-free, unfilled, and are suitable for small crack widths down to 0.1 mm on account of their low viscosity of 150–400 mPa·s. Epoxy resins should be workable for a sufficiently long period to enable them to penetrate into the smallest cracks. As their tensile strength and adhesion strength on the concrete is greater than the tensile strength of concrete, the component will fail outside of the injected crack in the event of overloading. EP can only be introduced into dry cracks.

6.5.1.2 PUR agents

PUR agents are used to seal cracks which move. They also consist of 2 components, are solvent-free and unfilled. In contrast to EP, PUR can also be used in damp and wet cracks, and even in cracks subject to water pressure. In order to achieve a seal of limited elasticity, the width of the crack must be at least 0.3 mm. If the crack only requires to be sealed, it may be narrower. A reliable seal is attainable when a maximum change in crack width of 0.05 mm applies for cracks of between 0.3 mm and 0.5 mm in width, or at a maximum change of 0.1 mm for cracks of over 0.5 mm in width.

6.5.1.3 Cement pastes and suspensions

On account of the required grinding fineness, cements corresponding at least to strength class C 42.5 in accordance with EN 197 or special injection cements are used for cement pastes (CP) and cement suspensions (CS). Cement suspensions are produced using ultra-fine cement with a specific surface area of up to 16 000 cm^2/g. The ultra-fine cement component consists of 95% purity with a grain size of <16 µm. In order to avoid segregation and sedimentation in the crack, the components must be thoroughly opened up by means of appropriate mixing and processing equipment. Cracks down to 0.8 mm width can be closed with CP, cracks down to 0.25 mm width with CS. CP and CS are unable to absorb crack movements after setting. CP and CS may be used on cracks containing any level of moisture. Their advantage over polymer crack-filling substances is that they possess the same fire resistance as the concrete component to be repaired.

Requirements pertaining to crack-filling substances are described in EN 1504-5. Key aspects for all crack-filling substances are:

- Adequate mixing stability (especially all for cement pastes and cement suspensions).
- Low viscosity, to enable penetration into narrow cracks.
- Adequate workable time, at both low and high temperatures.
- Low shrinkage (for resins).
- Good adhesion on concrete.
- Adequate tensile and compressive strength.

Specific requirements also apply to the different crack-filling substances. These include adequately fast strength development for epoxy resins and for polyurethane resins elasticity is especially important. The selection of a crack-filling material depends on the moisture content in the sides of the crack (dry, moist, unpressurised or subject to water pressure) and the objective of the measure (see Section 6.2.2). Cracks should ideally show their maximum width during filling. The workable time for a mixed filling material can be increased by cooling where ambient temperatures are high.

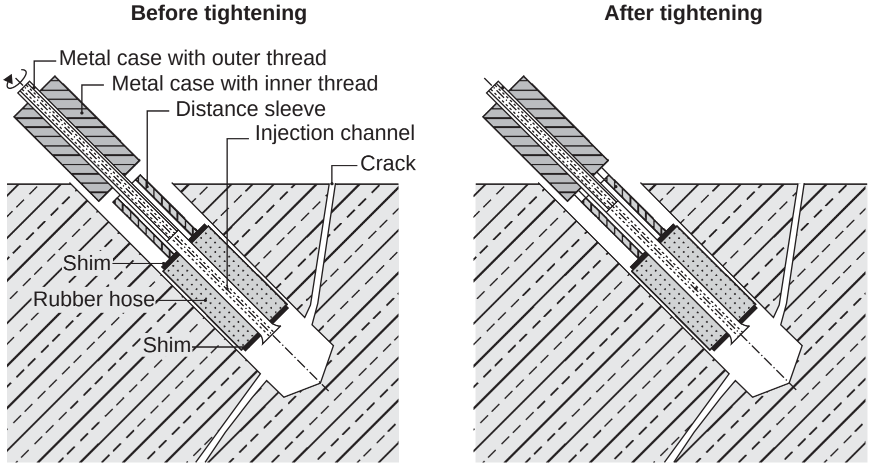
6.5.2 Crack-filling methods

Before filling, the cracks must be freed of loose fine matter, e.g. with a suitable vacuum cleaner. Depending on the level of moisture content in the concrete, the edges of the crack may need to be dried before treating the crack. With regard to the method of introducing the filling agent, a distinction is made between impregnation and injection.

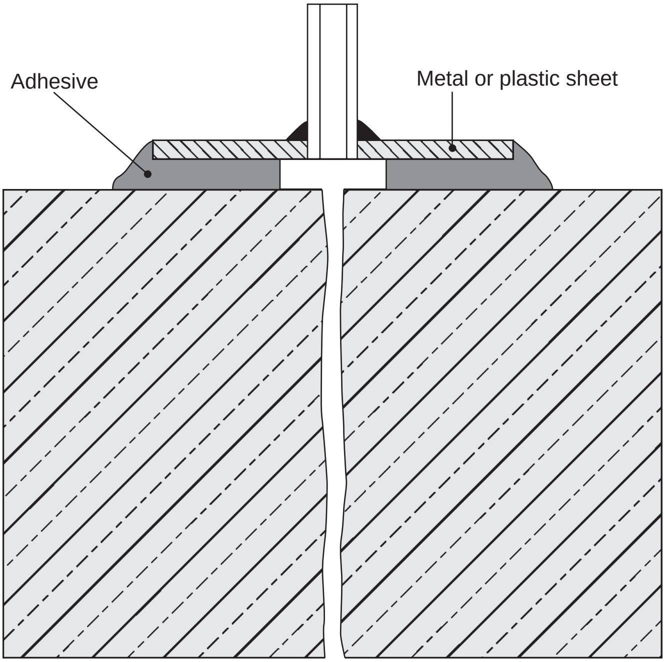
Impregnation is defined as the filling of cracks on (usually) horizontal surfaces from above at a maximum pressure of 0.1 bar. The impregnating agent penetrates into the crack as a result of gravity and the capillarity of the crack. Impregnation is generally only suitable for filling areas of cracks near the surface. This harbours the risk that the crack may only be partially sealed and may open up again in response to only minimal changes in the crack width. When impregnating, there must be an adequate supply of the crack-filling agent until it can be seen that the crack is unable to absorb any more of it. The impregnation of cracks on vertical surfaces is usually carried out with the aid of a brush, while on horizontal surfaces a flooding technique is often applied, using a rubber slide. Epoxy resins are ideal for impregnating very narrow cracks on account of their low surface tension.

In contrast to impregnation, injection methods aim to fill a crack completely. The filling agent is introduced under pressure with the aid of filling nozzles, which are known as packers. Common variants are bore-hole packers and adhesive packers. Bore-hole packers require a hole that is drilled at an angle of 45 ° and must cross the crack, see Fig. 6.6. Bore-hole packers are used for higher pressures and are equipped with a check valve. Adhesive packers are cemented onto the component over the crack by means of a plate, see Fig. 6.7. After applying the packers the crack is completely dammed up, usually by means of fast-setting cold-curing resin compounds. Injection into inclined components is always carried out in an upward direction from below. A ventilation opening is essential at the uppermost point. As soon as the filling agent issues from the next-highest filling nozzle, the injection process is continued at this nozzle. Irrespective of the type of filling agent, a follow-up injection should be carried out within the workable time, in order to compensate volume losses as a result, for example, of capillary effects or leaks.

So-called balloon and spring pressure packers have proved effective on account of the fact that a higher degree of crack filling is attainable at low pressure over a prolonged period than at high pressure over a short period. Balloon packers are not reusable and operate at a pressure of 3 bar, while the operating pressure of the reusable spring-pressure packers stands at 0.6 bar. When an appropriately long workable time is available, injection depths of 0.5 m are attainable with the latter method at a crack width of 0.2 mm.



6.6 Appearance of drilled packer before and after guying in the drilling hole.



6.7 Position of glued packer.

When cracks subject to water pressure are to be sealed with PUR, a preliminary injection of polyurethane foam, so-called secondary foam (SPUR), can be carried out, producing a fine-celled, large-volume foam to reduce the level of water inflow; this should be limited to the areas in which this is absolutely necessary. Attempts should be made to attain the highest possible level of filling with PUR. The PUR is injected by means of additional bore-hole packers directly after applying the SPUR.

6.6 Mortars and concretes

6.6.1 General

If the concrete is subject to local structural damage, as can be established by tapping the concrete surface with a hammer, for example, or if carbonated or chloride-contaminated concrete must be removed, the areas from which the concrete is taken must be closed again using a suitable material. Concrete or mortar are also used to increase the thickness of the concrete covering. The following materials are used as concrete supplements and substitutes:

- Concrete.
- Sprayed concrete.
- Cement mortar.
- Polymer-modified, cement-bound concrete or mortar (polymer cement concrete, PCC).
- Polymer-modified, cement-bound concrete or mortar applied by spraying (sprayed polymer cement concrete, SPCC).
- Cold-curing resin-bound concrete or mortar (polymer concrete, PC).

The requirements pertaining to the concretes and mortars are specified in EN 1504-3. The following requirements are significant:

- Compressive strength.
- Adhesion to the concrete.
- Shrinkage/swelling.
- Maximum chloride ion content.
- Carbonation resistance.

They must be fulfilled for all applications in the area of repair methods 7.1, 7.2 and 7.4. A distinction is made between two categories – 'of relevance to statics' and 'not of relevance to statics'. The concretes and mortars that are suitable for use in areas of relevance to statics are subject to different and higher requirements in terms of compressive strength and bond strength only.

6.6.2 Polymer-modified cement mortars/concretes

Cement is the main binder in SPCC and PCC. The solid polymer content ranges between 0.5 and 5 % in relation to the mass of the dry mortar. Higher polymer contents generally render the necessary alkalinity of the mortar/concrete (referred to henceforth as mortar) unattainable. In contrast to cement, polymer does not contribute towards alkalinity.

Thermoplastics are used almost exclusively for SPCC and PCC. Commonly used substances are acrylates, styrene–acrylate copolymers, styrene–butadiene copolymers, vinyl acetate co- and terpolymers, vinylidene chloride copolymers and vinyl propionate copolymers. The starting materials for PCC are delivered to the construction site either in two components (factory-produced dry mortar and polymer dispersion) or in single-component form (factory-produced dry mortar only); there is a clear trend towards single-component mortar. In addition to aggregate and cement, the factory-produced dry mortar may also contain additives and supplementary agents in powder form. The polymer dispersion may contain additives in liquid form (e.g. defoaming agents). In the case of single-component mortar, the polymer is admixed to the dry component at the factory.

Dispersion powders are generally used for SPCC; these are obtained by spray-drying dispersions. Not all dispersions are suitable for this purpose, however (e.g. styrene–butadiene). The polymer powder is converted back into a dispersion by adding water at the construction site. When the water is extracted from the dispersion (in the course of hydration of the cement and evaporation), the polymer particles stick together. This physical process is also referred to as film formation. A form of polymer network forms in SPCC and PCC when the solid polymer constituent stands at around 5 % of the cement weight or above. Epoxy resin is rarely used either for PCC or for SPCC.

The polymer component enhances the following properties of the cement mortar:

- Water-retention capacity.
- Tensile strength.
- Bond strength.
- Ductility.

While (a) reduces the sensitivity to poor curing, the combination of (a), (b) and (d) is responsible for the reduced susceptibility to cracking. All the properties together enable improved adhesion. In addition, thinner layers are possible on concrete substrates than are feasible with purely cement-bound mortars or concretes.

SPCCs differ from PCCs with regard to the mode of compaction: while PCCs are compacted by hand, SPCCs are compacted by means of the spraying energy. PCCs are sometimes conveyed to the area requiring repair by mechanical means (pumping). Rigid PCC is often compacted by means of machinery in the horizontal area, e.g. vibrating beam. SPCC is applied either by dry spraying or wet spraying. The dry spraying method involves adding the liquid (generally water) to the dry component in the nozzle. In the case of wet spraying, the ready-mixed mortar is conveyed to the nozzle. In the dry spraying method, the SPCC is applied to the surface with a higher level of energy than in the wet spraying method. SPCC is especially employed to increase the thickness of the concrete covering over large areas. The surface is often left untreated in its sprayed state but when the surface is to be smoothed, the SPCC is applied in at least two layers and only the second layer is smoothed.

PCCs are always used in conjunction with a bonding course, which is also cement-bound and which serves to ensure an adequate bond with the substrate. The bonding courses are similar to the PCCs in composition, but have a markedly smaller maximum grain size. PCCs and bonding courses are often referred to as substitute concrete systems.

6.7 Protective layers for concrete surfaces

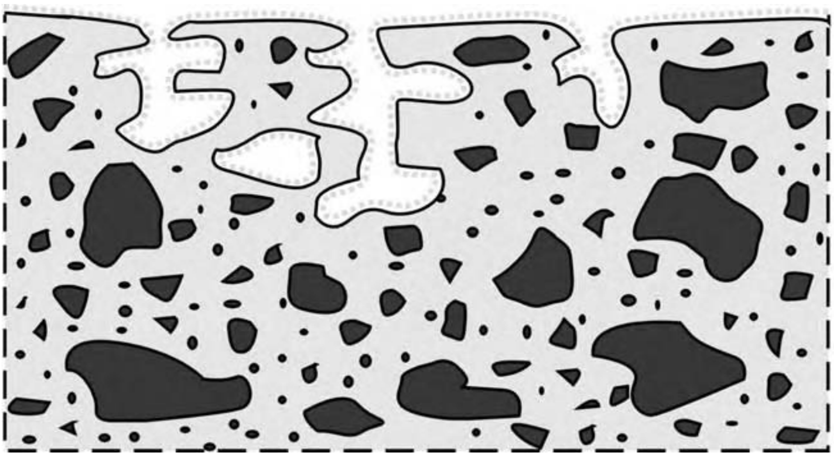
6.7.1 General

A distinction is made between three types of surface protection systems on the basis of their appearance: hydrophobic treatment, impregnation and coating.

6.7.2 Hydrophobic agents

Hydrophobic agents do not form a visible film on the surface of the concrete or mortar and have only a negligible effect on the latter's appearance. The pores are not filled, but merely lined, see Fig. 6.8. Penetration depths of up to 5 mm apply, according to the porosity of the concrete. Waterproofing layers consist of pigment- and filler-rich organo-silicon compounds in concentrations of 20 to 100 %.

The aim of hydrophobation is to render the surface of the concrete or mortar repellent to water. As a sole measure, it prevents the capillary intake of water, including entrained harmful substances. Surface soiling and colonisation by algae, moss and fungus are reduced. The penetration depth is crucial to the duration of effectiveness. The more deeply the hydrophobic agent penetrates into the substrate, the longer it will remain effective. However, as the effectiveness of hydrophobation is always of limited duration (as can be observed by the loss of the 'beading' effect displayed by the water on the concrete surface) it needs to be repeated from time to time. As one element of a surface protection system, water-proofing is intended to improve the long-term adhesion of a coating to the substrate.



6.8 Pattern of hydrophobic impregnation.

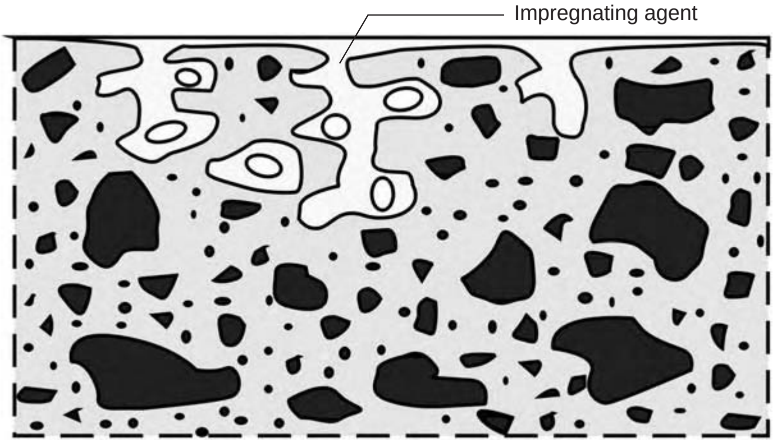
6.7.3 Impregnating agents

Impregnating agents serve largely to prevent the penetration of liquid or gaseous substances into the concrete. As primers, they are intended to improve the stability of the substrate or adhesion to the next layer. Impregnation leads to an uneven film of usually 10 to 100 μm in thickness on the surface; the pores are filled in most parts, see Fig. 6.9. Impregnating agents consist of low molecular substances on an epoxy resin, polyurethane or acrylate base, possess varying degrees of solvent content, but have no pigments and no fillers.

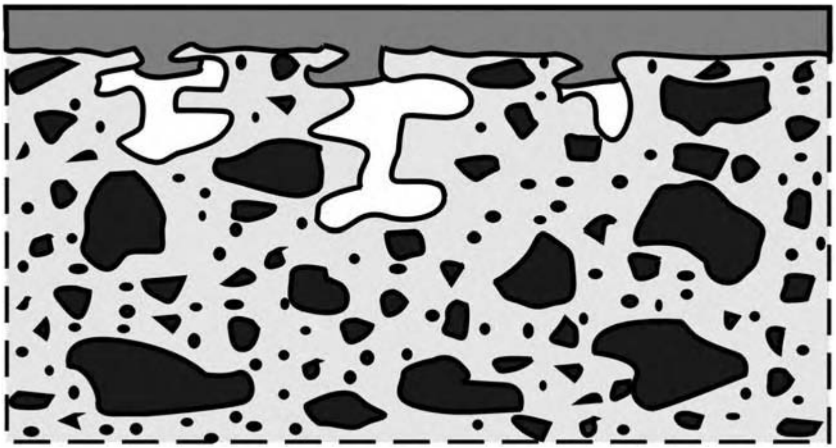
6.7.4 Coatings

6.7.4.1 General

Coatings serve to prevent or reduce the penetration of liquid and gaseous substances into the concrete, to protect the concrete from mechanical and chemical stress and to bridge cracks. They form a closed layer of 0.1 to 5 mm in thickness on the surface of the concrete, see Fig. 6.10. Thicker coatings may also be necessary for certain applications. Depending on the purpose of the coating, possible materials are cold-curing resins on an epoxy, polyurethane or acrylate base, or polymer dispersions and polymer-modified cement slurries that are filled to varying degrees. In this context, the term 'filled' refers to the use of an aggregate in the dispersion, generally quartz sand. With regard to the functions, a distinction is made between the following types of coatings: Levelling coats, primer coats, primarily active surface protection coatings and finish seals.



6.9 Pattern of impregnation.



6.10 Pattern of coating.

6.7.4.2 Levelling coat

A levelling coat serves to:

- Level the roughness of the concrete surface.
- Close pores, voids and gravel nests.

This enables the subsequent layers to be applied in a uniform layer thickness. Polymer-modified cement mortars are used predominantly for this purpose, with cold-curing resin mortars with a maximum grain size of 0.5 mm also being used in some instances, or with a grain size of up to 1 mm in isolated cases. The coat thickness may be up to 3 mm.

6.7.4.3 Primer coat

A primer coat serves to:

- Seal pores and prevent extraction of the binders from subsequent layers.
- Prevent the penetration of air, moisture and substances harmful to coatings (e.g. alkalis) from the substrate into the subsequent layers.
- Stabilise the substrate in the area near the surface.
- Produce a bonding course for the subsequent layers (possibly in conjunction with strewn particles).

Its structure corresponds to that of an impregnating agent and it should ideally be free of solvent content, in order to minimise the risk of blistering.

6.7.4.4 Primarily active surface protection coatings

The primarily active surface protection coatings (PAC) possess one or more of the following functions:

- Impermeability to water (combined with water vapour-permeability).
- Impermeability to carbon dioxide.
- Crack-bridging.
- Resistance to mechanical strain (wear resistance, resistance to stress induced by temperature changes).

These functions result in three types of PACs:

- Sealing surface protection coatings.
- Crack-bridging surface protection coatings.
- Wearing courses.

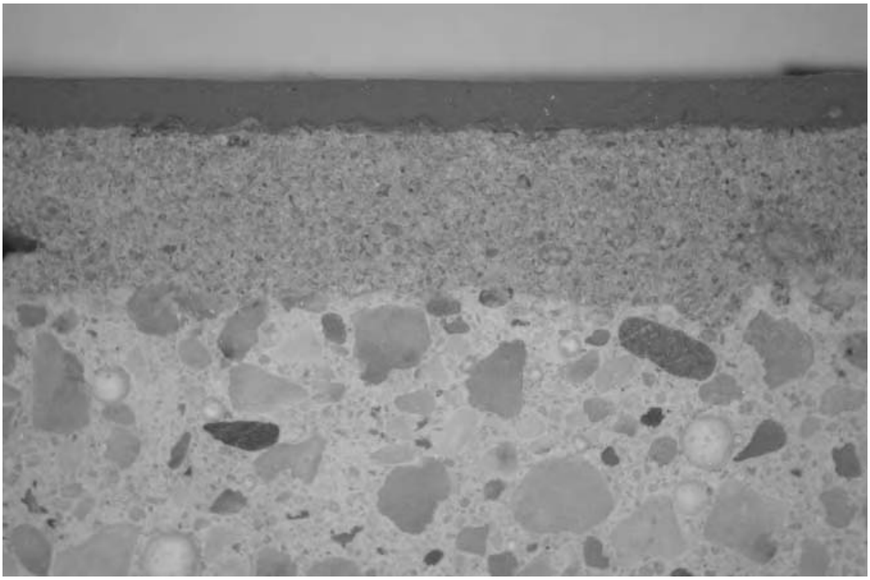
PACs usually consist of two layers.

The crack-bridging property of a coating is attained through elastification and/or adequate thickness. It is also possible to reinforce the coating with textile inserts, e.g. glass fabric. Wear courses do not generally serve any other function, as their rate of wear corresponds to their purpose. As a rule, they are additionally applied when the surface is subject to mechanical or chemical strain, e.g. when the surface is driven over. The sealing and crack-bridging function is more commonly performed by the layer underneath.

Wear courses are produced in a cold-curing resin mortar in free-flowing consistency in a thickness of up to 5 mm. Epoxy resin, polyurethane or 2-component acrylate are used as binders. The surface can be provided with a good grip by strewing on dry sand. As the hardness of the grain determines the wear resistance, silicon carbide or corundum is often used instead of quartz on surfaces subject to high levels of stress. A disadvantage of the surfaces containing strewn particles is their extreme susceptibility to soiling, particularly in areas that are not exposed to rain. The cleaning properties can be improved in roofed-over areas by means of a finish seal. The level of grip can be adjusted as required within a broad spectrum through the applied quantity of sealant. The strewn particles are also incorporated more effectively into the coating as a result of the finish seal.

6.7.4.5 Surface protection systems

Surface protection systems (SPS) consist of one layer (water-proofing, impregnation) or several such layers, the composition of which depends on the given requirements. Polymer dispersions or polymer-cement mixtures are employed for the PACs of SPS that possess a low crack-bridging capacity and are not intended for foot or vehicle traffic. As polymer–cement mix-



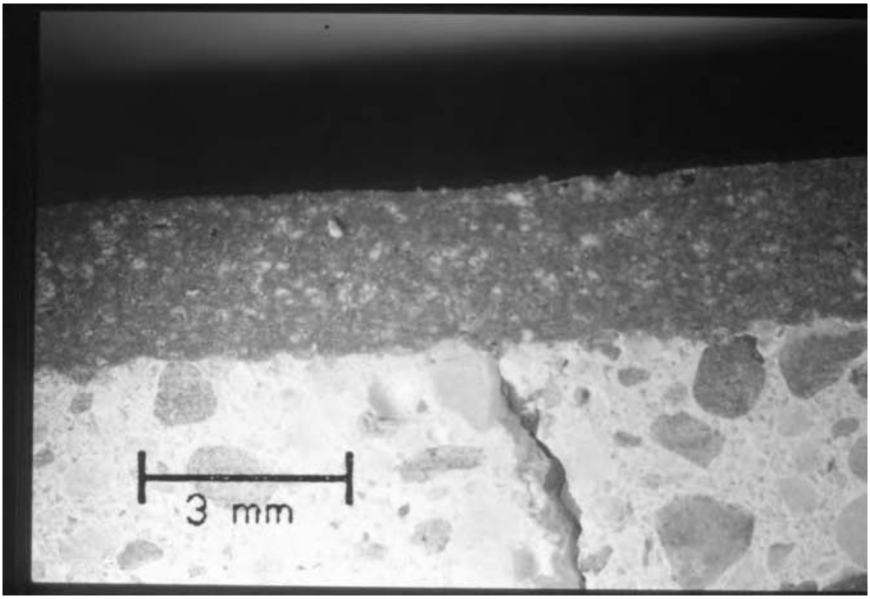
6.11 SPS with low crack-bridging ability, not for carrying traffic; composition: smoothing trowel, primer, polymer dispersion (300 μm).

tures tend to soil severely when exposed to the weather, a top sealing course is expedient. When using polymer dispersions, UV-curing acrylate dispersions have proved an effective means of preventing surface soiling as a result of stickiness. Figure 6.11 shows an SP system with a PAC consisting of a polymer dispersion, while Fig. 6.12 shows an SP system with a PAC consisting of a polymer–cement mixture.

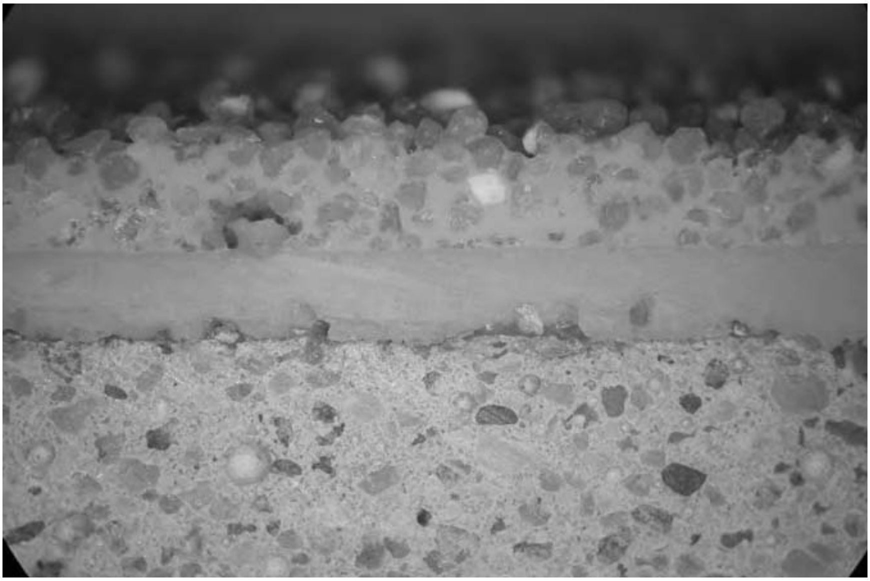
SPS that are to bridge cracks and are to be suitable for foot and/or vehicle traffic generally consist of two PACs. The lower PAC is elastic and is responsible for bridging the crack. The upper PAC, which is generally harder, serves as the wear course. Figure 6.13 shows a cross-section through such SPS. Polyurethane, epoxy resin and 2-component acrylate serve as binders for both layers. A rarer alternative is the SPS consisting of one PAC, whereby the elastic PAC performs both functions simultaneously. Polyurethane binders are used almost exclusively for such systems.

All requirements pertaining to SPS in general as well as in specific cases are stipulated in EN 1504-2 according to the respective repair methods. In addition to the above-stated requirements, adequate adhesion to the substrate also needs to be verified (see the section below on requirements pertaining to the concrete substrate).

With regard to crack bridging, a distinction is made between so-called static cracks and dynamic cracks. EN 1504-2 distinguishes between 5 classes of static cracks with crack widths ranging between 0.1 mm and >2.5 mm. The



6.12 SPS with low crack-bridging ability, not for carrying traffic; composition: primer, polymer cement mixture.



6.13 SPS with improved dynamic crack-bridging ability, for carrying traffic; composition: primer, elastic layer (1.5 mm), wear resistant layer (2 mm).

crack opening rates during preliminary testing range between 0.05 mm/min for narrow cracks and 0.5 mm for wide cracks. Six classes of test conditions apply for dynamic cracks. The crack width difference (i.e. between the largest and the smallest) ranges from 0.05 mm to 0.3 mm, while the crack-opening frequency ranges between 0.03 and 1 Hz and the number of crack opening cycles between 100 and 20 000. The test is normally carried out at –10 °C, but other temperatures can be used. Temperatures as low as –40 °C may be expedient in special cases.

6.7.4.6 Required layer thickness

The effective functioning of SPS hinges to a decisive extent on their overall thickness and the thickness of the PAC. The information regarding how the SPS are applied must therefore specify the thicknesses of the layers. The specifications always relate to the dried layer (dry layer thickness) and it is imperative that they are observed.

A distinction is made between the following terms with regard to layer thickness:

- Minimum layer thickness, d_{min}.
- Layer thickness additional, d_z.
- Target layer thickness, d_s.
- Maximum layer thickness, d_{max}.

The minimum and maximum thicknesses of the PAC are determined in the course of assessing the system's essential viability (initial type testing). The minimum layer thickness is the maximum value for the layer thickness which is necessary in order to:

- Withstand the stress resulting from thermal cycling.
- Pass the appropriate crack-bridging test.
- Attain the required CO_2 diffusion resistance.

In *Deutscher Ausschuß für Stahlbeton*, Part 2, Table 5.2 (see Section 6.9) values are given for d_{min} that have proved effective.

In order to ensure that the minimum layer thickness determined in the basic testing is also attained reliably in practice, an additional layer thickness, d_z, based on the type of SPS and the substrate roughness (peak-to-valley height) is expedient. The peak-to-valley height may be deter-mined by means of the sand surface method (see *Deutscher Ausschuß für Stahlbeton*, Part 3). The maximum layer thickness is the maximum thickness which is permissible in order to ensure the required water vapour permeability. The layer thickness (dry layer thickness) to be applied in practice must lie between the target layer thickness, $d_s = d_{min} + d_z$, and the maximum layer thickness.

6.7.4.7 Requirements pertaining to the concrete substrate

The substrate to which SPS are applied must possess adequate surface tension strength. In accordance with the adhesion strengths stipulated in EN 1504-2, Tables 4 and 5, for SPS on a defined concrete substrate, the mean values should lie between 0.1 MPa (vertical surfaces) and 2.0 MPa (hard systems intended for traffic). This applies both to old concrete and to the surfaces of concretes and mortars that are part of a concrete replacement system. The surface treatment of repair mortars may result in the formation of very thin layers on the surface that possess low surface tension strength (accumulations of dispersion and cement paste with high water content). In many cases it is therefore expedient to blast the mortar surfaces lightly, prior to applying SPS.

6.8 Coatings for steel surfaces

The following materials are used to coat steels:

- Cold-curing resin systems based on epoxy resins with low or no solvent content, to which anti-corrosion pigments (e.g. zinc phosphate or zinc dust) or fillers (e.g. fine clinker powder) or cement are added.
- Polymer-modified cement slurries.

Polymer-modified cement slurries have an advantage over epoxy resin systems in that the steel surface is not subject to such high requirements regarding cleanliness. High-pressure water-blasting is sufficient, while epoxy resin systems generally require particle blasting methods.

The required layer thickness for cold-curing resin systems is substantially less than for cement-bound systems. Cold-curing resin systems should be at least 300 μm thick in single- or double-layer configuration, whereby the first layer should be at least 200 μm thick. Quartz sand should be sprinkled over the upper layer, in order to improve the bond with the concrete replacement system. In the case of Method 11.2 (barrier coating) the first layer must never be sprinkled with sand, in order to avoid the risk of perforating the coating. When a sprayed mortar/concrete is used as the concrete replacement material, a 3-layer coating system may be expedient, as the spraying process has an abrasive effect on the coating. Cement-bound systems are at least 1000 μm in thickness.

6.9 Further reading

1 *Deutscher Ausschuss für Stahlbeton (DAfStb)*, Richtlinie für Schutz und Instandsetzung von Betonbauteilen (Guidelines for the protection and repair of concrete components); Part 1: Allgemeine Regelungen und Planungsgrundsätze; Part 2:

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Corrosion inhibitors for reinforced concrete

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7.1 Introduction

Corrosion represents the main reason for damage of reinforced concrete structures and the costs related to corrosion and repair work are significant. Therefore, there is a great need for cost-effective mitigation measures that help to stop corrosion or at least decrease the corrosion rate to a level that allows the structure the potential to reach the design life. In recent years, significant effort has been put into techniques to increase the service life of reinforced concrete structures. Among others, epoxy coating of the reinforcing steel, stainless reinforcing steel, hydrophobic treatment of the concrete surface, pozzolanic additives to the concrete, and corrosion inhibitors have been studied extensively.

Among all of these techniques, inhibitors represent an interesting approach to corrosion protection. They have been used successfully for several decades in numerous technical applications, such as process industry, heating and cooling systems, packaging, coating industry and many more. Moreover, they allow interaction with the corrosion process itself. Unlike techniques that are focused on preventing the aggressive substances from penetrating the concrete, inhibitors can offer corrosion protection when the aggressive substances are already present or even when corrosion is already initiated. As a consequence, inhibitors do not only offer a variety of corrosion protection strategies but also the possibility of application as a cost-effective repair strategy.

Corrosion inhibitors are defined as substances that affect the corrosion process by decreasing the corrosion rate; however, substances that decrease the corrosion rate by affecting the transport mechanism of the aggressive substances to the reinforcing steel are not corrosion inhibitors. The complexity of the corrosion process and difficulty in understanding the actual inhibition process often makes it difficult to differentiate between mass transport effect and actual corrosion inhibition. Therefore the discussion of corrosion inhibitors available or investigated for their application in concrete is not based on the above definition but on their definition in the literature or by the producer.

The application and the limitations of corrosion inhibitors is strongly affected by their chemical nature and their interaction with the concrete. While the addition to the admixing water offers numerous advantages, such as homogeneous distribution in the concrete, it requires that the inhibitor does not affect the concrete properties. Many inhibiting substances are known to decrease setting time or adversely modify the freeze–thaw resistance of the concrete. On the other hand, the surface application of the inhibitor on existing structures requires that the inhibiting substances exhibit high mobility to reach the reinforcing steel in a short time and at sufficiently high concentration to provide corrosion-inhibiting properties. Moreover, the processes for chloride-induced corrosion and for corrosion due to carbonation of the concrete are very different and require different inhibiting actions.

In order to select the correct corrosion inhibitor for a specific application it is necessary to understand the corrosion-inhibitive properties of the various substances used and the way they interact with the different types of corrosion. The discussion of the fundamental differences between the inhibitor types and the peculiar condition in the concrete allows us to understand the limitations of the use of corrosion inhibitors. Moreover, the discussion of the practical experiences reported in the literature provides the information required for the selection of corrosion inhibitors for specific practical applications.

7.2 Inhibition of corrosion with chemical substances

7.2.1 Introduction

Corrosion inhibitors are used in numerous technical applications with great success. A number of chemical substances are known to exhibit specific corrosion-inhibiting properties and their use allows the relatively simple and cost-effective control of corrosion. In many cases a significant increase in the lifetime of components can therefore be achieved. Considering the industrial significance of corrosion inhibitors and the generally excellent experiences with these substances, it is surprising that the use of inhibitors in reinforced concrete structures is still very limited and that there is significant concern over their use. To understand the difficulties encountered in the application of the corrosion inhibitors in reinforced concrete, a knowledge of the specific corrosion mechanisms and of the different inhibitive action of the various substances is required.

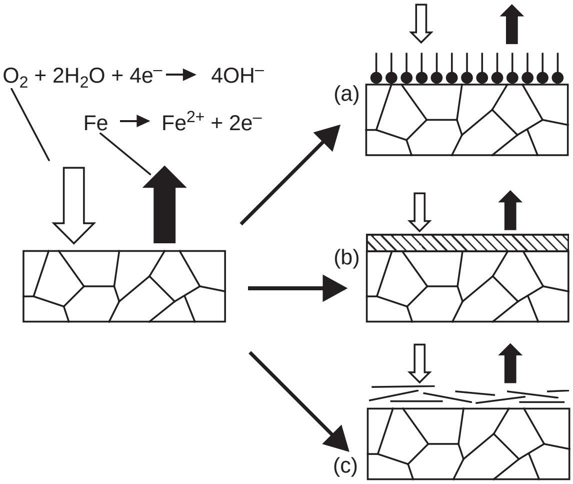
7.2.2 Corrosion inhibitors for uniform corrosion

In neutral and acidic solutions steel corrodes uniformly due to the lack of a protective passive film on the metal surface. As a consequence, the steel surface is homogeneously attacked resulting in a corrosion loss on the entire metal surface. Despite this lack of corrosion protection, steel is used in many technical applications such as heating and cooling systems, water supply and underground structures. The homogeneous metal loss allows us to estimate the expected lifetime based on empirical data. Moreover, the use of corrosion inhibitors has proved to be a cost-effective way of increasing the service life of such structures.

The classification of corrosion inhibitors is difficult because the detailed mechanism of the inhibitive action is not understood in many cases. Nevertheless, there are a number of general classes that can be summarised and help explain the fundamental properties of various substances.

7.2.2.1 Adsorption inhibitors

The electrochemical processes related to the corrosion process, such as cathodic reduction of oxygen and anodic metal oxidation take place on the metal surface. Substances that adsorb on the active sites of the metal and interfere with these reactions can significantly decrease the corrosion rate (Fig. 7.1a). These adsorption inhibitors attach to the metal either by



7.1 Inhibition of uniform corrosion: (a) Decrease of the corrosion rate by adsorption inhibitors; (b) Formation of a passive film due to passivators or passivation promoting inhibitors; (c) Decrease of the corrosion rate by cover-forming inhibitors.

chemisorption or physisorption and interact with either of the electrochemical reactions[1,2]. Often they are described as anodic, cathodic or mixed adsorption inhibitors, depending on the type of reaction they interfere with. Their ability to adsorb specifically on the metal surface generally results in extraordinarily small concentrations, in the range of 10^{-2} to 10^{-4} mol/l, being required for significant corrosion inhibition.

7.2.2.2 Passivators

The formation of a protective passive film on the steel surface is possible also at pH values below 10. However, a high corrosion current density is required for the passivation, which requires a sufficiently high concentration of oxidation agents in the electrolyte. Since the solubility of oxygen in the electrolyte is limited, the spontaneous passivation is only possible by addition of other oxidation agents, the so-called passivators. By increasing the dissolution current density above the critical current density for passivation, the spontaneous passivation of the steel is possible (Fig. 7.1b). Typical examples of passivators are nitrite, chromate, and oxygen[3]. Their concentration is often very low and can be in the range of 10^{-4} to 10^{-5} mol/l. The concentration of these passivators has to be continuously monitored, as a decrease of the inhibitor concentration to below the critical value required for the passivation of the metal can result in corrosion acceleration compared to the non-inhibited solution. The passivators are continuously consumed over time, resulting in a decrease of their concentration. Therefore a system without a continuous supply of the passivator is prone to end up with a concentration which is too low and so corrosion acceleration has to be expected in systems without control of the inhibitor concentration.

7.2.2.3 Passivation-promoting inhibitors

Another approach to providing corrosion protection of steel by passivation is to modify the electrolyte by adding passivation-promoting inhibitors. Those inhibitors generally decrease the current density required for the formation of the passive film to a degree, so that passivation is possible with the oxygen dissolved in the electrolyte (Fig. 7.1b). Most passivation-promoting inhibitors form iron salts of low solubility. Typical examples are phosphates, borates and organic acids. The same effect is also achieved by increasing the pH of the electrolyte above a value of 10. The concentration required for efficiency is in the range of 10^{-3} to 10^{-1} mol/l and is significantly higher than for other inhibitor systems. Unlike the passivators, no corrosion acceleration is observed when the concentration is below the critical value.

7.2.2.4 Cover-forming inhibitors

The electrochemical reactions occurring on the steel surface can be significantly affected by precipitates forming on the metal surface. They prevent the oxidising agent from reaching the metal surface or the dissolution reaction of the metal (Fig. 7.1c). There is a variety of cover-forming inhibitors that form a film on the steel surface and even on corrosion products slowing down the corrosion reaction. Typical examples are orthophosphates or low-soluble polyamines. These systems are generally used in water supply systems due to their non-toxic properties.

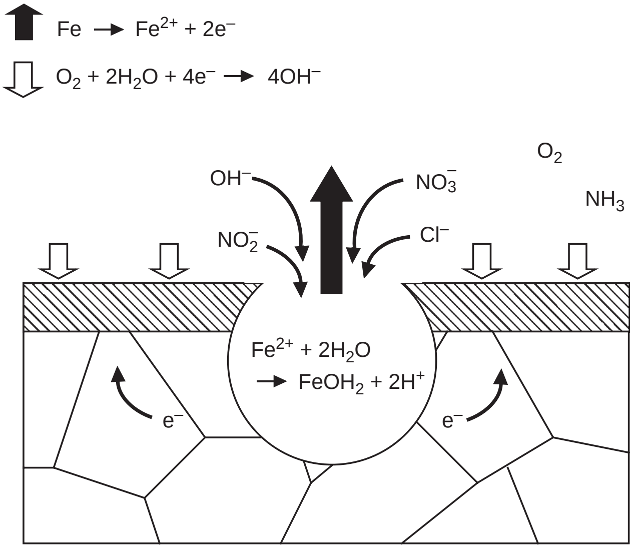
7.2.3 Corrosion inhibitors for localised corrosion

The formation of a passive film results in outstanding protection of steel against uniform corrosion. As long as the passivation-promoting inhibitor and the passivator are present, a virtually unlimited durability of the steel can be expected. However, passive systems are prone to localised corrosion in the presence of chlorides. This localised corrosion attack is associated with high corrosion rates due to the formation of a macro-element. Rapid dissolution is possible with local dissolution rates in the range of millimetres per year.

While the fundamental processes in the case of the uniform corrosion are quite well understood, the detailed mechanism of localised corrosion and its initiation are still subject to research. In order to understand the problems associated with the inhibition of localised corrosion, a knowledge of the fundamental aspects of activation, repassivation and stabilisation of localised corrosion is required.

The localised corrosion can be separated into different stages. The first step is the initiation of the corrosion. It is generally accepted that the initiation occurs on heterogeneities in the metal surface. Based on recent investigations the initiation takes place even in the absence of chlorides and is essentially governed by the number, geometry, and type of the heterogeneities[4]. In the next stage these initiation sites can repassivate. It is observed that the majority of the initiations sites repassivate within fractions of a second[5,6]. In these cases the corrosion is stopped. However, in some cases the corrosion attack can be stabilised, resulting in localised corrosion. The reasons for the stabilisation of the localised corrosion attack can be summarised as follows.

The metal ions dissolved due to anodic dissolution of the metal result in their hydrolysis in the water. As a consequence, the pH in the evolving pit decreases significantly (Fig. 7.2). The geometric conditions prevent the compensation of this acidification with the bulk electrolyte due to hindered mass transport. Hence the critical current density for passivation increases.



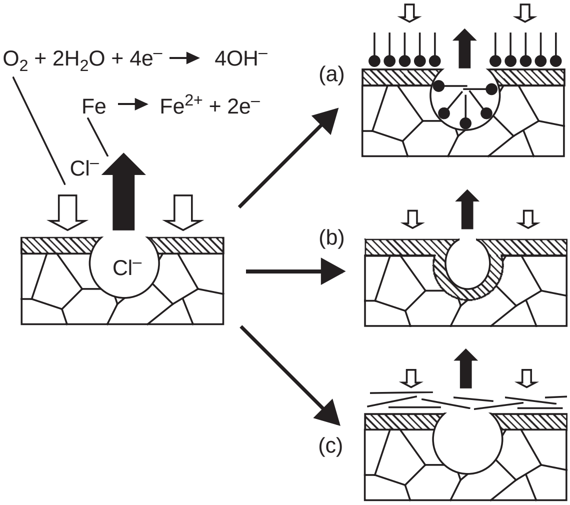
7.2 Processes during the evolution of pitting corrosion. The pH value in the pit is decreasing due to hydrolysis and negatively charged ions are migrating into the pit.

Meanwhile, the concentration of oxidising agents decreases, as the diffusion of oxygen into the corrosion site is strongly affected by the geometric conditions. The macro-element current results in the migration of anions, primarily chlorides and hydroxides into the pit (Fig. 7.2). There are additional processes that might be involved such as the precipitation of a salt film. However, the essential effects of the inhibition of localised corrosion can be understood based on this simple model.

The competitive migration of chlorides and hydroxides during the stabilisation stage of the localised corrosion allows the explanation of the experimentally observed relation between hydroxide and chloride concentration. Stabilisation of corrosion is observed when the quotient of the concentrations of chlorides to hydroxides exceeds 0.1. Hence, it can be concluded that at least part of this effect is due to competitive migration. A corrosion inhibitor that is able to prevent localised corrosion, that can stop it, or that at least can slow down the corrosion rate has to interact with this complex mechanism.

7.2.3.1 Adsorption inhibitors

By adsorbing chemical substances on the passive film and the formation of monomolecular layers the resistance against localised corrosion can be increased[7,8]. Primarily, the use of organic acids is reported to result in a strong adsorption and the increase of the corrosion resistance (Fig. 7.3a).



7.3 Inhibition of pitting corrosion of passive steel: (a) Decrease of the corrosion rate by adsorption inhibitors; (b) Repassivation of the pit due to passivators or passivation-promoting inhibitors; (c) Decrease of the corrosion rate by cover-forming inhibitors.

Part of the effect may be caused by a separation of the chlorides from the passive steel as proposed by DeBerry[7]. More recent results indicate that the adsorption of a monomolecular layer results primarily in the inhibition of the cathodic reduction reaction. By decreasing the cathodic current density, the macro-element and, therefore, the initiation process during stabilisation of the pitting corrosion are affected.

7.2.3.2 Passivators

The depletion of oxygen in the forming pit during the initiation of localised corrosion is one of the reasons for its stabilisation. Oxygen as a neutral molecule is only transported by means of the comparably slow diffusion process. By using anionic passivators the situation is significantly changed. The substance is transported into the forming pit due to migration (Fig. 7.2). The repassivation is therefore enhanced (Fig. 7.3b). Additionally, the inhibitor takes part in the competing migration between hydroxides and chlorides by decreasing the amount of chlorides transported. Typical passivators used are nitrites, chromates and molybdates.

7.2.3.3 Passivation-promoting inhibitors

Generally, the passivation-promoting inhibitors used against uniform corrosion also exhibit some positive effect in the case of localised corrosion.

These anions interfere with the migration of chlorides into the forming pit and decrease the critical current density for repassivation (Fig. 7.3b). Probably also the pH buffering effect of the typical passivation-promoting inhibitors, borates, phosphates, and of the hydroxides additionally supports the inhibitive effect.

7.2.3.4 Cover-forming inhibitors

The covering of the passive surface can prevent the access of the aggressive ions and therefore prevent corrosion initiation. Additionally, the covering of the surface can significantly decrease the cathodic current density and therefore interfere with the stabilisation process of the pit and decrease the corrosion rate (Fig. 7.3c). The protection mechanism is comparable with the one observed with the adsorption inhibitors. However, rather than a monomolecular layer a non-specific deposit is formed on the surface of the passive metal.

7.2.4 Corrosion inhibition in concrete

7.2.4.1 Introduction

The numerous experiences with corrosion inhibitors in aqueous solutions clearly demonstrate the efficiency of these substances in controlling corrosion. However, the conditions in concrete strongly differ from those in aqueous solution. When adding inhibitors to the mixing water they may not interact with the hardening process of the concrete. Therefore, there are limitations in the chemical substances that can be used. On the other hand, the application of the corrosion inhibitor on the concrete surface requires the penetration of the substance and its transport to the steel. Since concrete is an open system it is possible that the inhibitor is washed out or evaporates from the structure, decreasing its concentration and interfering with the environment in the case of toxic substances. Moreover, concrete is generally recycled and reused in other applications. Contrary to applications in closed aqueous systems, such as cooling circuits, the treatment or removing of the inhibitor is not possible. Hence possible leakage and interference in later applications cannot be excluded.

7.2.4.2 Interaction of chemicals with concrete

The addition of corrosion inhibitors to concrete results in an interaction of the two components. This interaction can affect either the concrete properties or the inhibitor efficiency or both. This effect is best illustrated by the example of benzoic acid, which is a good corrosion inhibitor in aqueous systems. The addition of benzoic acid to the mixing water of concrete results in a non-acceptable acceleration of the hardening process of the concrete. This substance could therefore only be applied on existing concrete structures. However, the benzoic acid forms salts of low solubility in solutions that contain calcium ions. Hence, fast precipitation is observed when applying the substance on concrete surfaces. As a consequence, benzoic acids and other carbonic acids are not suitable as corrosion inhibitors in concrete, although they exhibit good inhibiting properties.

Besides the interaction of the inhibitor with the concrete itself it has to be ensured that the numerous additives such as plasticisers, pore formers or hardening time controllers are not affected by the inhibitor or affect its efficiency. While the processes occurring in concrete are comparably simple and the relevant processes are well understood, the interactions with the additives are difficult to predict. Partly this is caused by the unknown composition and action of the corresponding products. Before using new formulations it is absolutely essential to contact the supplier or to run test batches to double-check the properties of the end-product.

7.2.4.3 Mass transport in concrete

Some substances exhibit good inhibiting properties but interfere with the setting process of concrete to such an extent that it cannot be compensated by modification of the concrete formulation. These substances can only be used as corrosion protection when applied on the concrete surface. In order to provide corrosion protection, a sufficiently high inhibitor concentration must be reached at the steel surface. This is only possible by a transport process that allows fast penetration of the corrosion inhibitor. In general, mass transport through concrete occurrs either by diffusion or by capillary action.

Diffusion is a comparatively slow process. Diffusion controlled mass transport only takes place under stationary conditions, such as in or on constantly submerged structures. Typically, the transport of chlorides in concrete immersed in sea water can be calculated according to Fick's law. However, in concrete structures exposed to changing weathering conditions, the mass transport is controlled by subsequent wet and dry periods. During the dry periods, the water content of the concrete is decreased, while the subsequent wetting with water causes a fast penetration of the components dissolved in the water into the concrete due to capillary action. Within one dry–wet cycle penetration depths of several centimetres can be observed[9]. During this process, not only the components dissolved in the water, but also soluble species in the pore system of the concrete are transported into the structure. Typically, chlorides present in the outer layer of the concrete accumulated during winter can be transported to the rebar in a subsequent wetting season.

This process clearly has consequences for the application of corrosion inhibitors on the concrete surface. A fast penetration of the inhibitor can only be achieved by wet–dry cycles. This is possible if the corrosion inhibitor is soluble in the pore solution of concrete. If it forms products of low-solubility, such as carbonic acids in the presence of calcium ions, a penetration of the corrosion inhibitor to the rebar cannot be expected.

It is well known that many corrosion inhibitors require an inhibitor concentration at the steel surface that is similar to or even higher than the chloride concentration[10]. When the inhibitor is transported by wet–dry cycles also the readily soluble chlorides present in the concrete are transported to the rebar. Hence, the amount of inhibitor has to match the chlorides accumulated over the service time of the structure. These can be significant amounts eventually requiring several surface applications of the inhibitor.

The use of volatile inhibitors offers an alternative and significantly faster transport mechanism through concrete. The high mobility in the gas phase allows fast penetration of the inhibitor into concrete. Primarily amines are known to penetrate concrete rapidly[11–13].

7.3 Application of corrosion inhibitors in concrete

7.3.1 Introduction

There are various ways of applying or introducing the corrosion inhibitor on the concrete structure. Its application depends not only on the expected corrosion risk, but also on the chemical properties of the corrosion inhibitor. While the adding of the inhibitor to the mixing water ensures homogeneous distribution throughout the concrete structure, it possibly affects the properties of the cement. Hence, the desired concrete properties, the expected corrosion risk and the specific inhibitor properties have to be considered in choosing the correct application.

7.3.2 Use of inhibitor as concrete admixture

Adding the corrosion inhibitor to the mixing water of concrete ensures homogeneous distribution of the inhibitor in the structure and solves one of the key problems of the inhibitor use in concrete. This mode of application brings the inhibiting substance to the steel surface prior to the ingress of the chlorides. In most inhibiting systems the concentrations of the inhibitor and of the chlorides have to be of the same magnitude to obtain sufficient corrosion protection and therefore the presence of the inhibitor in high concentration at the steel surface is expected to provide a maximum level of protection. Although this mode of application is probably the most reliable, there are some basic problems.

Adding the corrosion inhibitor to the mixing water is most likely to result in some interference of the inhibitor with the properties of the cement paste. Primarily, influences on the hardening process are observed. In some cases these effects can be corrected readily by adding retarders or accelerators. More complex and difficult to estimate is interference of the corrosion inhibitor with pore formers for increasing the freeze–thaw resistance or for adjusting the rheologic properties of the cement paste. This is especially true for inhibitors with surface-active components that are expected to interfere with these substances. Apart from the effect of the inhibitor on the cement paste, it has to be assured that the other concrete additives do not compromise the inhibiting properties of the inhibitor. Estimating the consequences of possible interactions does not only require profound chemical understanding of the chemical processes but also a detailed knowledge of the precise composition of the different components. The second requirement is especially difficult to achieve. In order to obtain maximum efficiency of the various components it is therefore recommended to obtain the advice of the provider of the inhibitor system or to obtain a complete system from a single source. This will allow maximum performance and especially allow the user to refer to the liability of the provider where performance is insufficient.

The adding of the inhibitor to the mixing water ensures homogeneous distribution in the concrete when installing the structure. Generally, it is observed that corrosion initiation occurs after a few years in the case of highly exposed structures. In other situations it can take several decades with the opening up of additional transport paths, such as cracks, before corrosion is initiated. During these years of exposure it must be ensured that the inhibitor is not washed out, consumed, or, in the case of volatile components, evaporated from the structure.

These problems are usually not recognised either in the product information of the corrosion inhibitors or in literature. However, to obtain the expected corrosion protection it is necessary to discuss these points with the supplier and consider guarantees from the point of view of corrosion protection.

7.3.3 Application of inhibitor on existing structures

7.3.3.1 Introduction

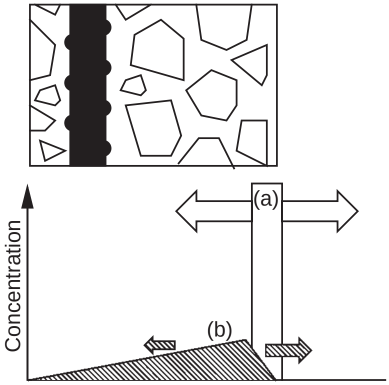
While the addition of the corrosion inhibitor to the mixing water of the concrete ensures the presence of the substance on the steel surface, it bears the risk of affecting the properties of the cement paste and possible long-term effects such as evaporation from the structure. However, the most crucial disadvantage is the additional cost of the concrete structure during construction. It is well known that proper concrete coverage, good concrete quality, sealing, or hydrophobic treatment can significantly decrease the risk of corrosion initiation. Therefore, the additional use of the corrosion inhibitor during the construction is only one possible alternative to other available methods. However, another interesting application of the corrosion inhibitor is its use for increasing the corrosion resistance of existing structures or even as a repair strategy in the case of structures with high level of chloride contamination and/or already occurring corrosion. Hence, the use of corrosion inhibitors could offer a promising low cost repair strategy for increasing the lifetime of existing or even damaged concrete structures without interfering with the concrete properties. However, in order to obtain sufficient corrosion protection, transport of the inhibitor to the rebar has to take place at a sufficiently high rate. Moreover, it has to be assured that the inhibitor does not only penetrate the concrete rapidly, but also remains present at the steel surface at sufficiently high concentration over long periods of time.

7.3.3.2 Transport of corrosion inhibitors through concrete

The only mechanism ensuring a sufficiently high rate of inhibitor transport through concrete is the capillary effect during wet–dry cycles or the transport through the gas phase. The inhibitor transport by capillary action can result in penetration depths of several centimetres within one cycle. However, for such a high transport rate optimal conditions from the point of view of humidity distribution in the concrete have to be present. It was found that such conditions are only present a few times a year[9] and for optimal transport the timing of the application is only possible in combination with a continuous monitoring of the concrete properties.

The transport rate observed with volatile corrosion inhibitors can also be considerable[11-14]. These high rates are related to the comparably fast diffusion in the gas phase. Humidity of the concrete is expected to be less critical than in the case of transport with capillary force. Despite the relatively simple mechanism of the transport processes, there are some problems related to them. Transport by either of the two processes will only take place if the inhibitor is soluble in the pore solution of the concrete; compounds forming low soluble precipitates in combination with calcium ions will not be transported. The precipitates will eventually close the concrete pores for further transport. A sufficiently high concentration of inhibitor at the steel surface will therefore be difficult to achieve.

Another problem associated with the transport process through the gas phase is the nature of the diffusion process. According to Fick's law the



7.4 Transport effect of surface-applied volatile corrosion inhibitors: (a) After surface application a strong concentration gradient promotes the transport of the inhibitor into the concrete; (b) After some time the rate of transport into the structure decreases due to a flattening of the gradient, while the strong gradient on the surface is maintained.

diffusion rate and direction depends on the concentration gradient and the diffusion constant. It is clear that any volatile inhibitor on the concrete surface (Fig. 7.4) can diffuse either into the concrete or into the gas phase. In order to obtain a sufficiently high concentration on the steel surface and to prevent significant loss of the inhibitor the evaporation into the gas phase has to be small; hence minimal evaporation into the gas phase is important to guarantee the long-term presence of the corrosion inhibitor in the structure and the durability of the corrosion protection.

7.3.3.3 Preventative strategy

The corrosion inhibitor can be applied on the concrete surface of an existing structure to obtain an inhibiting effect before the concentration of aggressive ions on the steel surface has reached critical values for the initiation of corrosion. The preliminary application has the advantage that the steel surface is still clean and not covered by corrosion products so that the interaction of the inhibitor can take place under ideal conditions. Moreover, most systems require an inhibitor concentration that is comparable to the chloride concentration to obtain an inhibiting effect. As long as the concentration of chlorides is still small, the inhibitor concentration on the steel surface can be increased to a significant level. Under certain conditions, the inhibitor applied on the surface is transported at the same rate as the chlorides to the steel surface, resulting in a protective effect when the chlorides reach it.

The application of the corrosion inhibitor on existing structures without corrosion damage is required when the inhibitor system adversely affects the properties of the cement paste or if the use of a corrosion inhibitor was not originally planned. Its application at a later stage might be indicated when the realisation of the structure deviates from the design, resulting in an increased corrosion risk. A typical case can be a concrete cover that is too small. The application of a corrosion inhibitor might compensate for the increased corrosion risk.

7.3.3.4 Application as repair strategy

The most important and interesting mode of inhibitor application is its use as a repair strategy. The large number of concrete structures subjected to corrosion damage and the significant repair costs related to them cause a high demand for cost-effective repair measures. The use of the corrosion inhibitor as a repair measure, however, presents some difficult problems. The chloride concentration on the steel surface has already reached the critical concentration for corrosion initiation and in most cases, the covering concrete is loaded with chlorides. Since the inhibitor concentration has to be in the same range as the chloride concentration, a high transport rate for the inhibitor is required. If the transport is based on the capillary effect, it will result not only in the transport of the inhibitor, but also of the chlorides present in the covering concrete, causing an additional increase of the chloride concentration.

The corrosion process on the steel surface has also resulted in the formation of corrosion products, representing an additional barrier for the inhibitor in reaching the steel surface. Generally, it is observed that the high chloride concentration and the hygroscopic effect of these chloride salts prevents the concrete from drying out and thereby decreases the effect of the capillary forces and transport through the gas phase. These problems may be primarily responsible for the lack of independent investigation available to date showing the efficiency of surface applied corrosion inhibitors.

7.3.4 Environmental aspects

The environmental aspects of the use of inhibitors to control corrosion and therefore increase the service life of concrete structures are complex and strongly depend on the specific composition and efficiency of the corrosion inhibitor system. As neither of these is known sufficiently well, a quantitative analysis of the environmental consequences of the use of corrosion inhibitors is not possible. Nevertheless, the basic aspects will be discussed.

The installation or traditional repair of a reinforced concrete structure requires significant amounts of resources and energy. If the use of a few per cent of additional chemicals can increase the service life significantly this represents a decrease in stresses imposed on the environment. Hence the estimation of the environmental effects is directly linked to the efficiency of the inhibitor and gain in service life.

Apart from this general perspective the use of toxic substances has consequences on the limitations for specific products. Most inhibitors are based on water-soluble or volatile products which means that they can be washed out of the concrete or evaporate. This process has not only consequences on the efficiency of the inhibitor but can also result in pollution of the environment. This consideration has led to the prohibition of nitrite in Europe due to its high toxicity and the possible environmental effects.

In the case of volatile components, environmental consequences for the waterways are negligible and the dilution of the small amounts evaporating from the concrete structure is large making the exceeding of any threshold values virtually impossible. However, for closed rooms with insufficient ventilation critical concentrations might be reached. Therefore, the use of volatile corrosion inhibitors requires special measures to prevent the presence of harmful concentrations in excess of what they should be. Since concrete is recycled and reused as an additive for new structures, the possible consequences of introducing components which might evaporate have to be considered.

7.4 Practical experience of corrosion inhibition in concrete

7.4.1 Introduction

Based on the discussion of the specific corrosion processes and the corrosion-protection mechanisms it is possible to explain the high corrosion resistance of steel in concrete. The high concentration of the passivation promoting inhibitor calcium hydroxide in combination with the passivator oxygen results in the formation of a passive film. From this point of view, steel in concrete has to be considered as a highly inhibited system, resulting in high durability. Nevertheless, severe corrosion damages have been found that led to the investigation of corrosion inhibitors against chloride-induced corrosion.

First results with corrosion inhibitors in concrete are reported with sodium benzoate[15] and chromates as admixtures for concrete. None of these inhibitors performed satisfactorily and some of them even had detrimental effects on the concrete properties. The efficiency of calcium nitrite as a corrosion inhibitor in concrete was first reported in 1977[16]. Since then, nitrite has been extensively studied and commercially used. More recently, various other substances have been investigated.

The commercially relevant inhibitors are discussed below from the point of view of available experience, their possible inhibition mechanism, and their limitations in specific applications.

7.4.2 Calcium nitrite

7.4.2.1 Introduction

Calcium nitrite has been used for corrosion protection in concrete for several years. It is added to the mixing water and has only limited effect on the concrete properties. No results with surface treatment of existing concrete structures are available. The efficiency of calcium and sodium nitrite as corrosion inhibitors against chloride-induced corrosion is reported in numerous publications[16–25]. The substance is capable of preventing corrosion in the case of chloride-induced localised corrosion and to decrease the corrosion rate after the onset of corrosion[26]. Based on this information, a critical ratio between nitrite and chloride has to be present in order to be efficient. This ratio is in the range of 0.5 to 1[10,27]. Considering that the chloride concentration can reach values up to 1 mol/litre within a few years on the level of the rebar under adverse conditions, very high inhibitor concentrations have to be present to ensure the long-term efficiency. The values required based on these observations are in the range of up to 6 % with respect to cement.

The investigation of the behaviour in repeated activation processes demonstrated the decrease of efficiency over time[26]; this behaviour can be explained by the consumption of the substance with each corrosion activation. While the inhibitor is consumed over time, the concentration of chlorides will increase over the years and it has therefore to be expected that the critical concentration for inhibition cannot be guaranteed in the long run. At too low concentration a corrosion acceleration is expected based on theoretical considerations[28]. Corrosion acceleration has indeed been observed for remedial treatment of concrete with nitrite[29].

In the case of carbonated concrete in the absence of chloride contamination an inhibitive effect of calcium nitrite added to the structure was found[10,30].

7.4.2.2 Protection mechanism

Based on experimental observations it is possible to draw some conclusions regarding the inhibition mechanism. The disappearance of the efficiency over time indicates the consumption of the nitrite and this explanation is based on the mechanism described for passivators. Due to its negative charge, the nitrite migrates into the pit where it promotes passivation by its oxidative properties. While increasing the cathodic current density it is reduced and its concentration, therefore, decreased. Moreover, the required high ratio between nitrites and chlorides indicates an effect of competing migration of the inhibitor into the pit during the initiation phase (Fig. 7.2). Hence, nitrite can interact with the corrosion initiation process directly and therefore delay the onset of corrosion. The high toxicity of nitrite has some impact on its application; for instance, in Europe it cannot be employed due to environmental regulations.

7.4.2.3 Application

Nitrite clearly shows an inhibiting effect on corrosion and must be added to the mixing water. Research carried out where the inhibitor was applied to the concrete surface as a repair strategy or to compensate for the consumption of the inhibitor over time only showed an inhibiting effect at low chloride concentrations[31,32]. Similarly, the addition of nitrite to the repair mortar did not yield any corrosion protection efficiency[33]. Apparently the ability of the nitrite to migrate through the concrete and reach sufficiently high concentrations on the rebar level is limited.

Nitrate is a natural by-product of nitrite. Since it can initiate stress corrosion cracking, there is concern that its presence might adversely affect the durability of high strength components such as tendons. Detailed investigation resulted in evidence that the concentration of nitrate is insufficient to present a possible risk for these elements[34]. In order to compensate for the problems related to cracks, the use of nitrite is recommended in concrete with a water-to-cement ratio of 0.4 and the additional use of polymer fibres to prevent cracking[35,36].

7.4.2.4 Summary

Nitrite clearly exhibits inhibiting properties in concrete against chloride-induced corrosion and carbonation when added to the mixing water. It is reported that it delays the initiation of corrosion and decreases the corrosion rate. However, its toxicity, the uncertain long-term behaviour and the problems observed in the case of cracked concrete limit its applicability. Based on the available data, the use of nitrite does not allow for compromise on the concrete quality and, hence, the additional costs for the inhibitor may not be compensated by cheaper manufacturing techniques.

7.4.3 Calcium nitrate

The laboratory investigation of concrete samples containing 4 % calcium nitrate with respect to cement over six years showed a delay of the corrosion initiation[37,38]. Hence, nitrate seems to have a comparable inhibiting effect as nitrite without its toxic properties. The inhibiting properties of nitrite with its oxidising properties[38] were explained in the previous section. In the presence of ferrous iron, which is formed during the corrosion process, nitrate is reduced to nitrite. Hence the corrosion inhibitor nitrite is formed from nitrate by a chemical reaction in the presence of corrosion products. In general, this reaction is relatively slow resulting in negligible concentration of nitrite. However, the observed inhibiting properties in concrete indicate that in the alkaline environment of the concrete the reaction is fast enough to provide corrosion protection. The additional reduction step increases the inhibiting capacity of nitrate compared to nitrite. The comparable corrosion inhibition mechanism suggests that also in the case of nitrate a critical ratio of nitrate to chloride is required. Moreover, the consumption of the inhibitor over time limits the efficiency.

Nitrate is added to the mixing water of concrete. Since it interferes with the hardening process, special measures have to be taken to compensate this effect. Nitrate is known to be capable of initiating stress corrosion cracking and there is concern that its presence might adversely affect the durability of high strength components such as tendons[39]. Nitrate seems to exhibit more inhibiting properties than does nitrite. Its reduction by ferrous iron is sufficiently fast at high pH values to provide effective corrosion protection of steel in concrete. It exhibits only limited toxicity and can therefore be applied in countries with strict environmental regulations.

7.4.4 Sodium monofluorophosphate

Sodium monofluorophosphate (MFP) was investigated as a corrosion inhibitor in the 1980s regarding its inhibition of chloride-induced corrosion[40]. According to this work, the ratio between MFP and chlorides must be at least one-to-one to show a certain decrease in the corrosion rate. Additionally, it was found that the inhibitor forms barely soluble products in combination with calcium ions. More recent work with application of the inhibitor on corroding structures did not yield any effect on the corrosion rate nor any repassivation in chloride-containing structures[9,31,41]. Similarly, no influence on the corrosion rate was found in carbonated concrete[31].

Since the pore solution of concrete is saturated with calcium ions, which form low soluble products with the inhibitor, the closing of the concrete pores is expected. It has been observed that this effect does not give any benefit when the inhibitor is used as a repair strategy on existing structures[41]. However, it might affect the transport process of chlorides after application on new structures and this could delay the initiation of chloride-induced corrosion. Another possible effect may be the increase of the pH due to the reaction of MFP with calcium ions[31]. MFP strongly affects the hardening process of concrete and, therefore, can only be applied to existing structures. There are no positive results reported when it is used as a repair strategy in field applications in chloride containing structures[41]. The available results do not indicate an actual inhibiting property of MFP when applied to concrete. Some beneficial results may be related to the delayed penetration of chlorides.

7.4.5 Hydroxyalkylamines

7.4.5.1 Introduction

There are several corrosion inhibitors currently available on the market that are based on hydroxyalkylamines and they have clear advantages over other corrosion inhibitors. Apparently the amine does not significantly affect the concrete properties when added to the mixing water. Moreover, it is volatile and exhibits high mobility in the gas phase. In contrast to other inhibitors it can penetrate concrete quite rapidly and has, therefore, the ability to reach relatively high concentrations[11,13,17] at the rebar level. Tests in simulated pore solution showed clearly the possibility of preventing initiation of pitting corrosion when present in sufficiently high concentration[42]. The addition of the inhibitor to the mixing water of concrete showed a delay of the corrosion initiation[42] on test samples in laboratory investigations. These results contrast with field investigations that did not show any significant efficiency of these products when added to concrete[18,33] or applied on the surface of corroding structures[41].

7.4.5.2 Protection mechanism

While laboratory investigations showed some efficiency of the inhibitors, investigations with pure hydroxyalkylamine did not yield any inhibiting properties[43]. A similar result was found by distilling the inhibitor and testing the volatile component[42]. According to the patent information of some products, the inhibitor consists of hydroxyalkylamines and carbonic acids[44]. In other cases the presence of inorganic phosphates is reported[31]. In general, it can be assumed that the efficiency of this product class is a result of the synergistic effects of carbonic acids or phosphates with the amines. The limited information available does not allow a detailed understanding of the inhibiting properties. It was demonstrated[42] that the non-volatile component, which contains the carbonic acids, strongly inhibits the cathodic reduction reaction, presumably by adsorption or precipitation on the metal surface. On the other hand, the amines have some effect on the anodic reaction. This inhibiting effect could be attributed to some pH buffering effect during the initiation of pitting corrosion. The single components were found to have only limited efficiency.

Based on this information it is possible to draw some conclusions regarding the expected efficiency of the inhibitor when used as a repair strategy. It was shown that the amine exhibits high diffusion rates in concrete[11–13]. This is related to its volatile nature that allows for fast transport through the gas phase. However, the efficiency of the corrosion inhibitor is only observed when both the volatile and the non-volatile components are present. The non-volatile components, which often consist of organic acids or phosphates, result in the precipitation of low-soluble components when added to calcium-ion containing solutions. Hence it must be doubted whether the non-volatile constituent of the inhibitor is capable of being transported through the pore solution of concrete which is saturated in calcium hydroxide. So far no independent investigation of the corrosion inhibitors has found a significant effect on the corrosion rate when the inhibitor was applied on the concrete surface of corroding structures[11,31,41].

While the expected slow transport of carbonic acids may be responsible for the lack of efficiency of the inhibitor when it is applied to the concrete surface, the high mobility of the amine possibly limits the durability of the protecting effect of the inhibitor when added to the mixing water. The high mobility of the inhibitor found in concrete[11–13] could result in evaporation of the substance from the structure and such evaporation was observed on reference samples[11]. This process could decrease the efficiency of the inhibitor over the years, while the evaporation of the toxic amine could offer a potential threat to humans. An inhibiting effect was not observed in the case of carbonated structures either when added to the mixing water or in surface application[31].

7.4.5.3 Application

According to the manufacturers, the corrosion inhibitors based on hydroxyalkylamines can be added to the mixing water without significantly affecting the properties of the concrete. The inhibitors can also be applied on existing concrete structures to increase lifetime expectancy and delay the initiation of corrosion. The inhibitor can also be applied on corroding structures to decrease the corrosion rate. The independent investigation of the efficiency of the corrosion inhibitor showed some inhibiting effects when it was added to the mixing water. No efficiency was reported when the substances were applied on the existing structures.

7.4.5.4 Summary

A detailed discussion of the corrosion inhibitors based on hydroxyalkylamines is not possible because the exact composition of the products is not known. Furthermore, the product names and presumably their composition have changed in recent years. Based on the available information most of these products consist of hydroxyalkylamines and added components such as carbonic acids or phosphates.

They all show some inhibiting effect when added to the mixing water. However, pozzolanic substances turned out to be clearly more efficient than these inhibitors[18]. The application of the corrosion inhibitors on the concrete surface did not result in a significant decrease of the corrosion rate in any independent publication.

There are no long-term studies available that predict the evaporation of volatile substances from concrete and their effect on inhibitor efficiency and possible adverse effects of toxic substances on humans.

7.4.6 Silanes

Recently the use of organofunctionalised alkoxysilanes is described for the corrosion protection of reinforced concrete structures[45]. Silanes have been applied on concrete surfaces for several years providing corrosion protection by making the surface hydrophobic, strongly decreasing the water uptake, and drying the concrete. The results available so far[45] show a pronounced ability of the product to decrease the corrosion rate when applied on new or already corroding concrete surfaces. In the case of already corroding structures, no repassivation has been found, but the corrosion rate was found to decrease for up to one order of magnitude.

The typical application of the inhibitor is performed on existing concrete structures, either to prevent or retard the initiation of corrosion or to decrease the corrosion rate of already actively corroding structures. The application of the product corresponds to hydrophobic treatment and can be performed by spraying.

Only little is known about the corrosion inhibition mechanism. It is expected that part of the observed decrease of the corrosion rate can be attributed to making the concrete surface hydrophobic, the drying of the concrete, and the increase of the electrical resistance. So far, no proof of the penetration of the molecules onto the steel surface is given. However, it is argued that the comparably small alkoxysilane molecules are highly mobile and can easily penetrate the concrete. Moreover, it is well known that silanes can interact and decrease the corrosion rate of steel[46]. The available information shows a promising behaviour of the product in decreasing the corrosion rate; these results are based on empirical investigations. It is unclear whether the observed corrosion inhibition is related to an actual interaction of the substance with the steel surface or to the drying of the structure. In the second case the inhibiting effect would only be expected if the structure is not in contact with soil (e.g. tunnel wall) or if the treated surface is undamaged. Because of a lack of practical information, the use of the product can be recommended in combination with a monitoring of the corrosion development. The low costs related to the repair work compared to conventional techniques justifies these additional expenses.

7.5 Summary

While the use of corrosion inhibitors is of technological importance in aqueous systems, their application in concrete has not yet resulted in a breakthrough in efficiency. This is mainly related to the strongly hindered mass transport process in concrete, to the presence of calcium ions that form low-soluble salts with many inhibiting substances and to the fact that concrete is an open system allowing washing out and evaporation of inhibiting substances.

In general, some inhibiting properties were found when substances were added directly to the mixing water of concrete. While this procedure ensures the homogeneous distribution of the inhibitor in the structure, possible interference with the concrete properties must be considered and compensated for. For this reason, a profound understanding of the composition of both inhibitor and concrete additives as well as of possible interference reactions is required. Since these are not generally available, test batches are needed or the recipe has to be approved by the supplier of the inhibitor to avoid possible negative effects on the concrete properties or on the inhibiting efficiency. While certain inhibiting systems show some effect in the case of addition to the mixing water, no independent proof of the efficiency of any surface-applied corrosion inhibitor as a repair strategy is available to date. Improvements in composition or the combination of corrosion inhibitors with alternative protection systems such as those with hydrophobic properties offer promising solutions for cost effective corrosion protection. However, various aspects affecting the long-term efficiency such as washing out or evaporation from the concrete structure have barely been addressed so far.

The lack of understanding of the inhibiting effect, the dependence of the corrosion process of external factors, the high cost related to a repair and the safety aspects related to the structure represent a significant risk for the owner of the structure and the supplier of the inhibiting product. Therefore the use of a corrosion inhibitor is only recommended in combination with an independent control of its efficiency. It is important that the effect of the corrosion rate is directly measured, for example by means of a corrosion monitoring system. In this case the owner has control of efficiency of the repair work and possible evidence to take issue with the supplier of the product in the case of failure.

7.6 Sources of further information

In the present chapter only limited information about the detailed protection mechanism of inhibiting substances has been presented. The actual status of research and development is described in conference proceedings on this topic[47,48] and Kaesche gives a description of the processes involved[49]. While these sources give detailed information about the behaviour of corrosion inhibitors in acidic and neutral solutions, only limited information about experience with corrosion inhibitors in concrete is available to date. A comprehensive and independent review on this topic so far has only been given by Page et al.[31]

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8

Electrochemical techniques for corrosion protection and maintenance

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8.1 Introduction

Corrosion protection of steel reinforcement in concrete can be lost due to ingress of chloride ions or carbonation of concrete. Conventional methods for concrete repair aim at removing all chloride-contaminated or carbonated concrete, cleaning the steel and reprofiling the surface with new, chloride-free and alkaline, cementitious concrete or mortar. In general, this is a cumbersome procedure that involves heavy labour and produces large amounts of noise, dust and waste material. Unless all chloride is removed, in particular from the steel surface including the inside of corrosion pits, corrosion may re-initiate after a short time. Consequently, conventional repairs can be expensive and may not be durable. During the last decades, electrochemical maintenance methods have been introduced which overcome these disadvantages of conventional repair (COST 521, 2003).

8.2 Types of electrochemical techniques available

One possible electrochemical method is cathodic protection (CP), which requires a permanently installed electrode material on or in the structure and a permanent current flow of low density (Pedeferri, 1992, 1998; Page, 1997; Polder, 1998a,b). CP reduces the corrosion rate by depressing the steel potential, which neutralises the corrosive effect of chloride ions or carbonation. Consequently, chloride-containing and carbonated concrete can be left in place. Application of current in cases where corrosion has not yet started is termed Cathodic Prevention (CPre), which will be discussed alongside CP.

Another method is electrochemical chloride removal (ECR) that is also called electrochemical chloride extraction (ECE) or desalination, which removes chloride from contaminated concrete by passing a direct current of a relatively high density for a limited period of time (Mietz, 1998). The aim of ECR is to suppress corrosion of reinforcement by reducing the chloride content of the concrete to below corrosive values.

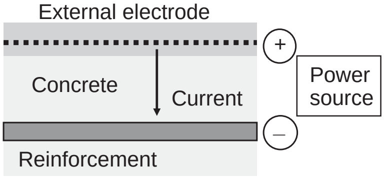
The third method, electrochemical realkalisation (ER) restores the alkalinity of carbonated concrete by passing an electrical current through concrete for a limited period of time (Mietz, 1998). Electrochemical reactions introduce hydroxyl ions into the concrete. After ER the alkalinity in the vicinity of the reinforcing steel is as high as or even higher than that of newly cast concrete and the corrosion is stopped by repassivation of the steel.

8.3 Common principles of the electrochemical techniques

The three electrochemical maintenance methods have principles and practical details in common. The main differences are the amount of current flowing through the concrete and the duration of the treatment as given in Table 8.1. A general set-up that is valid for all electrochemical methods is shown in Fig. 8.1. By means of an external conductor, the anode (⊕), a direct current is made to flow through the concrete to the reinforcement which thereby is made to act as the cathode (Θ) in an electrochemical cell. The current flow mitigates or stops the corrosion by repassivation of the rebars due to (1) polarisation of the reinforcement to a more negative potential, or (2) by removing the aggressive ions (chloride) from the pore solution in the concrete or (3) by reinstating its alkalinity. The following paragraphs explain briefly the physico- and electrochemical processes involved in electrochemical maintenance methods.

Table 8.1 Typical characteristics of electrochemical maintenance methods

Method	Duration	Typical current density
Cathodic protection	Permanent	10 mA/m^2
Realkalisation	Days to weeks	1 A/m^2
Chloride removal	Weeks to months	1 A/m^2



8.1 Schematic illustration of electrochemical maintenance methods.

Polarisation

Electrochemical methods work in part by making the potential of the reinforcement more (homogeneously) negative, thereby stopping or reducing corrosion to an acceptable value. Polarising the potential to more negative values and thereby depressing the corrosion rate is the main effect and objective of cathodic protection. Unlike the case of steel in sea water, the potential does not need to be depressed as low as 'protective' potentials (–850 mV CSE) due to the beneficial effects of the concrete cover such as its alkalinity.

Electrolysis

Current flow in concrete causes electrochemical reactions at the electrodes (anode, cathode), generally termed electrolysis. Electrolysis produces hydroxyl ions at the cathode by one of the following overall reactions:

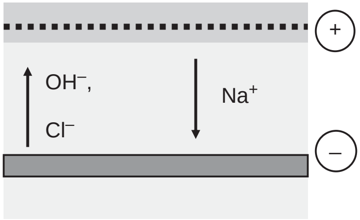
$$\text{oxygen reduction:}\quad O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad [8.1]$$

$$\text{water reduction:}\quad 2H_2O + 2e^- \rightarrow 2OH^- + H_2 \qquad [8.2]$$

Which of these reactions occurs depends on the availability of oxygen at the steel, which is related to the current density and the moisture content of the concrete. At low current densities and in well-aerated (semi-dry) concrete, reaction 8.1 is dominant. At high current densities and/or if the concrete is (near) water saturation, insufficient oxygen can reach the steel to sustain reaction 8.1 and consequently mainly reaction 8.2 takes place. Such conditions cause the steel potential to become very negative. Furthermore, the hydrogen produced may invoke the risk of hydrogen embrittlement of high strength steel. It should be noted that for every electron passed, the same number of hydroxyl ions is produced. This causes an increase of pH in the pore solution close to the reinforcement, thereby contributing to both repassivation of the steel and to a higher critical chloride content (the amount of chloride that initiates corrosion). This production of hydroxyl ions at the steel by electrolysis is one of the effects and objectives of realkalisation.

Electromigration

Negatively charged ions will move from the steel towards the positive electrode (the anode) and positively charged ions move towards the negative electrode, the reinforcement (Fig. 8.2). Together this flow of ions carries the current through the concrete. The ions participate in this migration process in relative proportion to their transport numbers; the transport number of



8.2 Flow of ions (electromigration) in an electrical field in the concrete cover.

a given ion is a function of its mobility and concentration. In concrete pore solution most of the current is carried by hydroxyl ions, alkali metal ions and by chloride ions if present in significant amounts (Elsener, 1990; Andrade, 1993; Polder et al., 1995; Castellote et al., 1999a,b). Transport of chloride from the steel to the anode by migration is the main effect and objective of chloride extraction.

Electro-osmosis

Electro-osmosis is the transport of liquid in a porous material due to an applied electrical field. The rate of transport depends on the properties of the liquid, of the solid and the potential applied (Banfill, 1994). Electro-osmotic flow of alkaline liquid, in particular sodium carbonate solution, into concrete assists repassivation of the steel, which is one of the main effects of realkalisation. Electro-osmosis in concrete has been documented during realkalisation of carbonated concrete; it does not seem to occur in alkaline concrete (Andrade et al., 1999), for which the reasons are not completely understood.

8.4 Common practical aspects

Before repair or maintenance of a concrete structure is undertaken, a condition assessment must be made. Its objectives are to determine the current state of deterioration (causes and extent), the probable future rates of deterioration, the consequences involved and the requirements for repairs – now or in the future – with respect to both type and extent of repair. Any structural problems should be signalled at this stage and treated accordingly (Schiessl, 1994; Broomfield, 1997). When the condition assessment has shown that taking maintenance actions is necessary, repair options should be considered, including electrochemical methods. Application of electrochemical methods in practice is usually initiated by a preliminary investigation of the structure to be repaired. If electrochemical maintenance is anticipated, the preliminary investigation may be combined with the condition assessment.

From the information obtained and taking into account the requirements of the owner and users, a decision is made regarding the repair method. Some information that assists in making such decisions is given below. If an electrochemical method is chosen, a design is made and a specification is written. A company is selected to carry out the work. In the execution phase, various checks are made. For chloride removal and realkalisation the execution represents the actual anti-corrosion treatment. For CP, the execution phase occurs when the structure is prepared; the protection starts when the current is switched on after finishing the installation. In all cases, maintenance is required. The following paragraphs address some practical aspects common to the three methods.

Preliminary investigation

A preliminary investigation of the structure should include a general survey, identifying the presence of structural cracks, deformations and other obvious defects. If such defects are present at a significant level, the treatment should be reconsidered and structural repairs carried out. Where structural repairs are unnecessary, the inspection should focus on the preparation for electrochemical treatment. The following items should be assessed over representative parts of all areas to be treated.

Concrete cover to the steel

Measure the cover depth, its minimum, average and variation. It should be noted that a large variation in cover will cause corresponding non-uniform current distribution to the reinforcing steel. If cover variation is very large, special measures must be taken and it may be impracticable to apply electrochemical methods. Spots with low cover may need to be corrected before electrochemical methods can be applied successfully.

Chloride content and distribution

Determine the chloride profile, its variation across the concrete surface and the source of the chloride. Potential mapping will indicate the chloride distribution along the concrete surface (Elsener et al., 1993). The chloride distribution is important as the determination of the suitability of chloride removal is based on this. It is more difficult to remove chloride present behind the first layers of rebars; in general, removal of mixed-in chloride is less likely to be successful (Polder and Hondel, 1992). Identifying locations for process control cores in this stage is advisable.

Depth of carbonation

The carbonation depth should be measured at many locations. It is advisable that both carbonation depth and cover thickness are measured in the same spots for a rather large number of locations in order to allow a statistical evaluation of their distribution (Elsener et al., 1998; COST 521, 2003). Identification of locations for process control cores at this stage is advisable.

Electrical continuity of the reinforcement

The reinforcing steel must be electrically continuous for successful application of electrochemical methods. Discontinuous bars do not receive current, so they are not protected and may be subject to stray current effects causing accelerated corrosion. Discontinuities have to be corrected by providing additional connections. If a structure contains many disconnected rebars, it may be impracticable to apply these methods. It is stressed, however, that electrical continuity can be provided during the execution of the repair work. This obviously requires planning and additional cost.

Electrical continuity of the concrete

The concrete around the steel as well as between the steel and the anode has to provide continuous electrolytic conduction. This means that the concrete should not contain major cracks, delaminations or old repairs with a high electrical resistivity (e.g. non-cementitious polymer mortar repairs or coatings) because these may hinder uniform current flow. All such causes of non-uniform current flow must be checked and corrected before the application of the process.

The presence of potentially alkali-reactive aggregates

Because all electrochemical methods will increase the alkali content around the rebar to some extent, locally ASR expansion may be stimulated (Sergi et al., 1991; Page and Yu, 1995). The reactivity of the aggregate should be checked; if it is potentially reactive, a trial project is advised. This is valid for all the electrochemical methods although the changes of and causes for increased alkali content are different. According to recent studies carried out (COST 521, 2003), alkali–silica reaction is most unlikely to be a problem in re-alkalised carbonated concrete but is a potentially significant problem in ASR-sensitive concrete treated by chloride extraction. With CP, ASR is only a potential problem when much higher than normal current densities are applied for longer times (Sergi et al., 1991; Page, 1992).

The presence of prestressing steel

Due to the negative polarisation, hydrogen may be evolved at the steel surface. This is an important consideration for chloride extraction. With this method, the polarisation is very strong and the process duration is relatively long (it can be a matter of months). If prestressing steel is strongly polarised, this may induce hydrogen embrittlement and eventually sudden fracture. Post-tensioned steel in perfect ducts will be shielded from strong polarisation. In actual structures, defects in the ducts may occur and the risk may be real. Pretensioned steel in direct contact with the concrete is likely to be strongly polarised with ECR and RE. It should also be noted that some types of prestressing steel are more sensitive to hydrogen embrittlement than are others. Because of the high risk of structural damage, application of electrochemical chloride extraction to prestressed structures is not recommended unless trials have shown that no damage to the prestressing steel can occur. Such trials should be carried out by independent specialists.

The polarisation required for CP is much lower. With regard to the application of CP to prestressed structures, the prestressing steel is safe as long as the potential is more positive than –900 mV Ag/AgCl, according to the European Standard for cathodic protection of reinforced concrete (CEN, 2000). This requires specific monitoring, e.g. by embedding reference electrodes near the prestressing steel (Polder, 1998a,b) and careful current control. It is likely that by proper design and execution, CP of prestressed concrete structures is safely possible in many cases.

Determination of active regions of corrosion

Those zones where the reinforcement is actively corroding should be determined by means of non-destructive electrochemical techniques such as corrosion potential and corrosion rate mapping (Elsener et al., 1998; Andrade and Alonso, 2001). Sensors (e.g. reference electrodes) for monitoring the effect of electrochemical treatment should be placed in active areas.

Design, execution, maintenance

Considerations for design, tests during execution, and subsequent maintenance are treated separately for the three methods in the following sections.

Quality management

The application of an electrochemical treatment should comply with a quality management system. It means that each stage (design, installation, commissioning, operation, decommissioning) should be documented. The owner of the structure should agree with the quality management system proposed by the applicator before the start of the treatment.

Criteria for success of the treatment

For cathodic protection, a European Standard and several national documents exist (Concrete Society, 1989; CUR 1996; CEN, 2000). They specify criteria that are supported by long term practical experience. On CP installations, these criteria should be adhered to. For electrochemical chloride removal and realkalisation no accepted criteria or standards exist and it is therefore important to define and agree on the criteria of success of the treatment for any site job.

8.5 Cathodic protection

8.5.1 Mode of action and application

Cathodic protection (CP) of reinforcing steel has been applied to a large number of concrete structures with corrosion damage for over 25 years. World-wide experience shows that CP prevents further damage in a reliable and economical way for a long time. CP is particularly suitable in cases where chloride contamination has caused reinforcement corrosion. Application started in the USA in the 1970s on bridge decks suffering from corrosion due to deicing salt penetration resulting in severe damage to the concrete. Since the 1980s, CP has been applied to buildings, marine structures, tunnels and bridge decks and substructures in the USA, Europe and elsewhere in the world. New anode materials became available, of which in particular activated titanium and conductive coatings have proved their good performance. A further development is the application of CP to new structures where corrosion is anticipated within the service life, termed cathodic prevention. Recently a European standard was published (CEN, 2000). By the year 2000, cathodic protection had been applied to about 2 000 000 m^2 of reinforced concrete on a few thousand, at least partially, corroding structures.

Cathodic protection is based on changing the potential of the steel to more negative values, reducing potential differences between anodic and cathodic sites and so reducing the corrosion current to negligible values. The change of potential is called polarisation. In practice, this is realised by mounting an external electrode, the anode, on the concrete surface, connecting it with the positive terminal of a low voltage direct current source, while connecting the negative terminal to the reinforcement cage. Through the reinforcement cage, electrons flow to the steel–concrete interface, increasing the cathodic reaction, which produces hydroxyl ions from oxygen and water. The hydroxyl ions migrate through the concrete cover to the anode where they are oxidised to oxygen and electrons. The electrons flow to the current source, which closes the electrical circuit. As a result of this current circulation, cathodic reactions at the steel are favoured and anodic reactions are suppressed. Relatively moderate current densities are able to restore passivation and have various beneficial chemical effects. The required polarisation makes CP a permanent method: the current must flow during the remaining service life of the structure. For a uniform distribution of the protection current, the steel must be electrically continuous and the concrete must have a reasonably homogeneous conduction. Short circuits between the anode and the steel must always be avoided.

8.5.2 Anode materials

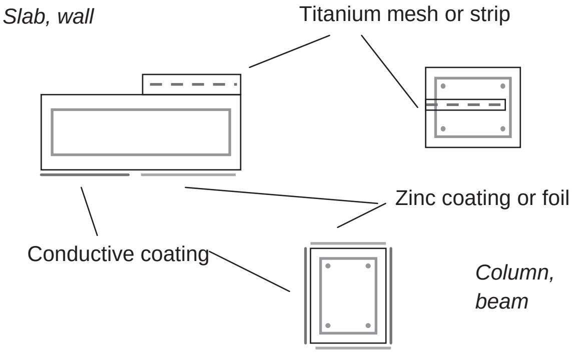
The centre of any CP system is the anode material, which comes in various forms:

- An electro-active mesh shaped to fit the surface of the structure and subsequently covered with a cementitious overlay.
- A set of wires or strips placed in holes or slots and backfilled with a cementitious grout.
- A conductive and electro-active coating covering the concrete surface.
- Carbon fibres in various shapes, including woven mats embedded in polymer-modified cementitious overlays.

Activated titanium expanded mesh with a surface coating of precious metal oxides is the most widely used and successful type of anode. It can be easily fixed to all surfaces, and is overlayed with a cementitious material, such as shotcrete (vertical or overhead surfaces) or flowable concrete (horizontal surfaces). The strip and wire systems involve inserting activated titanium strips or wires into holes drilled or grooves cut into concrete elements, that are then filled with cementitious grout. In general, titanium systems have the ability to deliver a relatively large protection current without compromising their durability.

Conductive organic coatings are solvent based or water-borne products, containing graphite particles to provide conduction. A series of metallic conductors is embedded in the coating to feed the current. A cosmetic top coat of normal concrete paint is applied. The adhesion depends on appropriate surface preparation and a suitable application technique. This type of anode can be applied to complex shapes in any orientation and presents no addition of weight. Over the past 15 years, conductive coatings have been shown to provide a service life expectation of over 10 to 15 years.

In Fig. 8.3, example sketches are given for the position of various anode systems with regard to the cross-section of concrete elements. Figure 8.4 shows three stages of application of titanium mesh to the underside of a concrete slab with corrosion due to penetrated chloride from sea water splash and waves.



8.3 Sketches of anode systems relative to the concrete cross-section.

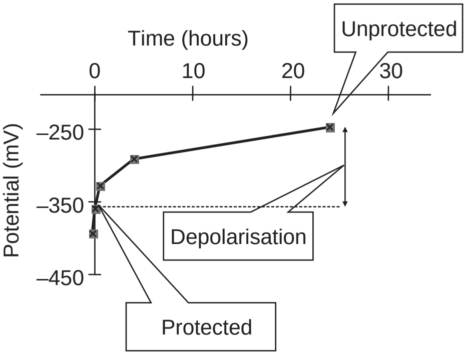
8.4 Three stages of application of a titanium mesh to the underside of a concrete slab with corrosion due to penetrated chloride; *left part of photo*: prepared surface; *middle*: titanium mesh attached (note big repair patch and plastic fixing pins); *right*: shotcrete overlay applied.

8.5.3 Monitoring of cathodic protection

The quality of protection offered by a CP system must be monitored by testing regularly, normally a few times each year. As a general measure of the quality of cathodic protection, the amount of polarisation that actually takes place in the structure is measured: as long as CP causes a certain minimum amount of polarisation, the corrosion is suppressed to an insignificant level. This is tested for by interrupting the protection current and monitoring the subsequent change of the steel potential over periods up to 24 hours at several representative points in the concrete structure using embedded sensors (decay probes or reference electrodes). With the current switched off, the steel potential relaxes from polarised to non (or less) polarised as shown in Fig. 8.5; this type of measurement is called depolarisation or decay test. Empirically, a minimum depolarisation of 100 mV over a period of 4 to 24 hours is considered indicative of sufficient protection for atmospheric concrete structures (CEN, 2000). For submerged or buried structures other criteria are applied, in particular a fixed negative potential limit (Linder, 1994).

8.5.4 Cathodic prevention

Cathodic prevention (CPre) has been applied to large motorway bridges in Italy and to various other structures where early depassivation and corrosion were anticipated (Pedeferri, 1992; Bertolini et al., 1996). Although the principle is the same as for CP, CPre can be achieved more easily: it is easier to prevent pitting corrosion than it is to suppress ongoing pitting corrosion. This means that less current density is required and that ‘prevention current’ spreads deeper into the structure than ‘protective current’ does.



8.5 Depolarisation of steel potential versus an embedded reference electrode or decay probe as a measure of the quality of cathodic protection.

Consequently, CPre systems can be designed and executed more simply, less anode material is needed, and/or their service life is longer. Installing anodes while a new structure is being built is much cheaper than installing them in an existing structure. CPre is monitored in the same way as is CP; however, the results are even more reliable due to the effects mentioned above. A mix of cathodic protection (of existing elements) and prevention of new elements in the same structure is also possible (Tettamanti et al., 1997).

8.5.5 Sacrificial cathodic protection

In the last decade, another type of CP has been developed for concrete that is based on sacrificial dissolution of less noble metals, such as zinc and zinc–aluminium alloys. The metal is applied onto the concrete surface by flame spraying, as a mesh or sheet adhering via a conductive gel. It is then short-circuited with the reinforcement and the natural potential difference between the zinc and the steel causes a current to flow. Sacrificial installations can be simple (they do not need an external power source); however, they do not provide a means of increasing the current or voltage in cases where the protection is below the criterion, e.g. 100 mV depolarisation.

Another matter is the service life of such systems, which depends on the amount of sacrificial material provided and the current density. Another application in this area is that of embedding blocks of zinc in repair patches which are electrically connected to the rebar, intended to prevent steel just outside the patch to start corroding (Sergi and Page, 1999).

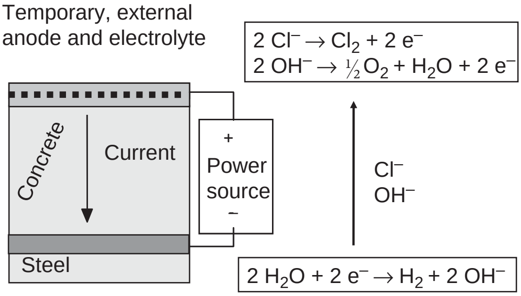
8.5.6 Closing remarks

A large body of experience with structures in various environments all over the world has shown that CP is very effective in stopping corrosion of reinforcement even if aggressive conditions continue to be active. This has been documented in many case studies of successful application of CP, concerning tunnels, bridges, floor elements, foundations, balconies, parking decks, façade and floor elements (Wyatt, 1993; Polder and Nuiten, 1994; Chaudhary and Chadwick, 1998; Haldemann and Schreyer, 1998; Leggedoor and Schuten, 1998; Polder, 1998a,b; Broomfield, 2000; Schuten et al., 2001; Nerland and Polder, 2002). An increasing number of structures with carbonation-induced corrosion has been provided with CP, in particular in Norway and The Netherlands. Technical guidance is given in International Standards and other documents (Concrete Society, 1989; NACE, 1990; CUR, 1996; CEN, 2000). Recently, the durability of CP systems has been investigated. From a study on samples taken from structures after up to 9 years of operation, a proprietary conductive coating system was concluded to have a service life of well over 10 years, possibly up to 20 years (Polder et al., 2001b). Experience and test results show that activated titanium systems have service lives well beyond 25 years (Polder et al., 2002). For the near future, a wider application of CP and CPre is expected, as well as the introduction of new anode materials and further development of sacrificial systems.

8.6 Electrochemical chloride removal

8.6.1 Mode of action and applications

The aim of electrochemical chloride removal (ECR) is to suppress corrosion of reinforcement by reducing the chloride content of the concrete to below corrosive values. A temporary anode is fixed to the concrete surface (usually a mesh of activated titanium or regular steel bars), surrounded by an aqueous electrolyte (usually a solution of calcium hydroxide or tap water); and a direct current of about 1 A/m^2 of concrete surface is passed between the anode and the reinforcement from a transformer/rectifier for a period of between several weeks and several months. The principal set-up and electrode reactions are shown in Fig. 8.6. By taking control cores and analysing their chloride content, the progress is monitored and the end-point of the treatment is determined. Subsequently, the anode and the electrolyte are removed and the surface is cleaned. No permanent installation is necessary, except monitoring devices if desired. This method has been applied to many structures over the past 15 years with usually positive experience. Disappointing results have been obtained, however, with removal of mixed-in chloride. Since the mid 1990s, the experience with and understanding of chloride extraction has expanded significantly. Various case studies (Tritthart, 1995, 1996; Elsener et al., 1998) and laboratory experiments have been described (Bennett and Schue, 1990; Polder, 1996;



8.6 Set-up of electrochemical chloride extraction with electrode reactions and ionic flow indicated.

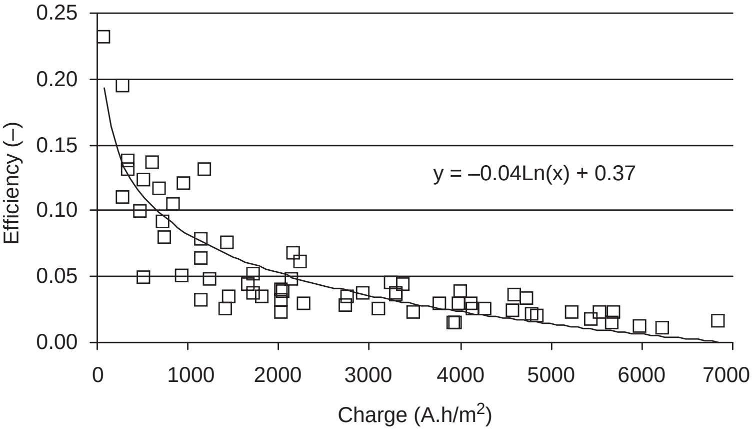
Vennesland et al., 1996; Polder and Hondel, 2002). General guidelines for application (COST 509, 1997) and a state-of-the-art report (Mietz, 1998) were published. By the year 2002, chloride extraction had become current practice with good success for cases of penetrated chloride, using impressed current as described here. Improvement is considered possible with regard to the economic side and non-destructive testing methods and criteria for effectiveness (COST 521, 2003). The use of sacrificial anodes, where a base metal provides the electrical energy and no external power is needed, seems to be a promising development (Raharinaivo et al., 1998a,b).

Unlike CP with its permanent current supply, successful ECR requires that the treatment achieves a protected situation that is durable without further intervention. Consequently, the most important questions are: how long should ECR be carried on for an acceptable result and how can the absence of corrosion for a longer period after finishing the treatment be obtained?

8.6.2 Effects of charge and of time

The treatment time is strongly related to the maximum current density. In general, the amount of chloride removed is proportional to the integral of current and time, which is the total electrical charge passed. Higher current densities would reduce the process time, but may cause negative side-effects (COST 509, 1997). Laboratory studies have shown the adverse effects of high current densities during longer times, in particular for the bond between steel and concrete which may deteriorate due to softening of the hardened cement paste. This is possibly due to accumulation of large amounts of alkali (sodium, potassium) ions near the steel and the high hydrogen gas pressures that arise (Vennesland et al., 1996; Chang, 2002). Loss of steel–concrete bond was observed in experiments involving pulling out ribbed bars from cylindrical concrete specimens subjected to strong polarisation. For instance after a polarisation of one month at 4 A/m^2, a 7 to 15 % loss of bond strength was found. The results suggest that current densities significantly higher than 1 A/m^2 of steel surface should be avoided in order to avoid loss of bond between reinforcement and concrete. Due to the inhomogeneous nature of concrete, local current densities may be several times higher than the average. Because of the risk associated with high *local* current densities at the steel surface, *average* current densities significantly higher than 1 A/m^2 should not be applied.

Studies have also shown that for increasing amounts of charge, the efficiency of chloride removal decreases (Bennett and Schue, 1990). The effect is illustrated in Fig. 8.7, showing the efficiency of the chloride removal (moles of chloride removed from the concrete per mole of electrons passed) during ECR treatment of specimens described below (Polder and Hondel,



8.7 Decrease of efficiency of ECR with increasing amount of charge passed.

2002). It is clear that for more than 2000 A.h/m^2 of charge, the efficiency decreases to below 0.1. This means that only 10 % of the current serves to move out chloride ions, or that the transport number of chloride has become as low as 0.1. This is due to the high concentration of hydroxyl ions produced at the steel by reaction 8.2. Due to the decreasing efficiency with charge, it may be necessary to repeat the treatment after some time to get the desired result (Elsener et al., 1998).

Figure 8.7 also indicates that a large amount of scatter is present in the test results (obtained from slabs of 0.3 × 0.3 m^2. In practical cases a similar level of scatter should be expected. This suggests that a relatively large number of samples must be taken to establish the effect of ECR, either for monitoring the process or for end-point determination, with reasonable reliability.

8.6.3 Durability of protection

The other issue is the durability of the achieved protection. In the short term, hydroxyl ions production at the steel and displacement of chloride from the steel certainly suppress corrosion (Polder et al., 1995). After stopping the polarisation, however, the hydroxyl ions that have accumulated at the steel will diffuse away relatively quickly. Because some chloride ions inevitably remain in the concrete, in particular between and behind bars, they will redistribute and may come back at the steel in corrosion-inducing levels after some time (Stoop and Polder, 1999). Obviously, this depends on the spatial distribution of chloride remaining after CE, its transport rate and the critical chloride content.

It appears to be difficult to obtain a final situation in which the average chloride content is below 0.4 % by mass of cement, which may be considered a safe value for long term absence of corrosion. Because of the partly inevitable scatter in the results, the amount of charge needed to obtain such a safe situation is impractically high, generally more than a few months at high current densities. Situations with a higher *average* chloride content than 0.4 % may be tolerated, however, if it can be shown that during a reasonable period of time, the chloride content *at the rebar* will not become higher than 0.4 %. This approach has been worked out by assuming that chloride redistribution takes place and can be modelled as diffusion (Stoop and Polder, 1996; Polder and Hondel, 2002).

8.6.4 Conclusions from experiments

A large number of concrete specimens were tested with initially about 2.5 % (penetrated) chloride by mass of cement in the outermost 15 mm and about 0.6 % from 15 to 30 mm (Polder and Hondel, 2002). They were made with either Portland or blast furnace slag cement, for which chloride diffusion coefficients were well known (Polder and Larbi, 1995). Starting from the chloride distribution profiles observed after ECR experiments and assuming that it should take at least 10 years after the ECR treatment before the chloride content at the rebar surface exceeds 0.4 % chloride by mass of cement, it was concluded that:

- For Portland cement concrete, at least 2400 A.h/m^2 (concrete surface) is required to obtain a sufficiently low remaining chloride profile, provided the minimum cover depth is 15 mm; this is equivalent to 100 days at 1 A/m^2.
- For Blast Furnace slag cement concrete, the required charge depends on the cover depth to the rebars; for cover depths of 15 to 20 mm, 2230 A.h/m^2 is required; for cover depths 20–25 mm, 1130 A.h/m^2 is needed; for cover depths over 25 mm, about 1000 A.h/m^2 is required (about 42 days at 1 A/m^2).

From similar laboratory experiments it was furthermore found that the following ‘defects’ that may be present in the concrete do not significantly reduce the effectiveness of ECR:

- Bending cracks with widths at the surface up to 0.6 mm (for other reasons, cracks wider than 0.2 mm are usually sealed).
- The presence of rebars with varying minimum cover depths between 15 and 30 mm.

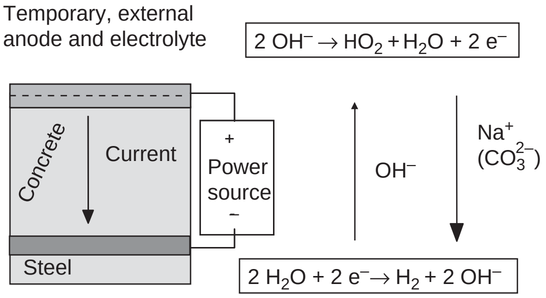
- The presence of tie wires protruding from the rebars until a few mm from the treated surface (obviously, short circuits between the anode and the reinforcement should be avoided).
- A low cement content (250 kg/m^3).

Potential measurements and chemical analysis of corrosion products from specimens with active pits strongly suggest that chloride is removed from inside the pits and that their corrosion activity is reduced considerably. In contrast to ECR of penetrated chloride, various experiments and practical cases have shown that it is much more difficult to remove mixed-in chloride, probably mainly for geometrical reasons. Even after long treatment times, too much chloride remains in the concrete to achieve a durable protected situation.

8.7 Electrochemical realkalisation

8.7.1 Mode of action and applications

Electrochemical realkalisation (ER) is a method to stop reinforcement corrosion induced by carbonation. The pH around the steel is increased and the passivating properties of the concrete pore solution are restored. ER involves passing a current of about 1 A/m^2 through the concrete to the reinforcement by means of a temporary anode on the surface. The set-up and electrode reactions are shown in Fig. 8.8. In the original application, a paste of sprayed cellulose with 1 molar solution of sodium carbonate is used as the electrolyte covering the concrete surface; the anode is a steel mesh. Nowadays, activated titanium anodes and tanks with liquid electrolyte are also used. The treatment lasts for between a few days and a few weeks. By taking control cores and analysing their pH, the progress of the process is monitored and the end-point of the treatment is determined. Subsequently,

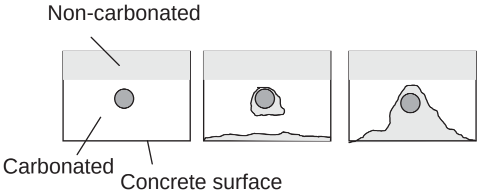


8.8 Set-up and reactions for electrochemical realkalisation; sodium and hydroxyl ions migrate due to current flow, carbonate supposedly moves in due to other processes.

the anode and the electrolyte are removed and the surface is cleaned. No permanent installation is necessary, except monitoring devices if desired. Realkalisation with impressed current was introduced by Noteby in the late 1980s (Noteby, 1987). In various countries, particularly in Norway and the UK, several hundred thousands of square metres have been treated. A variant of this technique was recently developed by Ciment d'Obourg and Freyssinet. The main difference is that the current is obtained from a sacrificial anode (Pollet et al., 1997). Because after the treatment the original concrete surface is left unchanged, realkalisation may be particularly suited for structures with special architectural values such as monuments.

Through various mechanisms (electro-osmotic flow, electromigration, diffusion and capillary absorption), alkaline species are transported into the concrete while electrolysis produces alkaline species at the steel surface. There has been some debate about electro-osmosis. No evidence of its occurrence has been found in laboratory tests or in field demonstration projects (Polder and Hondel, 1992; Mietz, 1998; Pollet, 1999). On the other hand, recent laboratory experiments by Andrade and co-workers (Andrade et al., 1998) have confirmed the occurrence of electro-osmosis, supporting similar observations by Banfill (1999). Electro-osmotic flow was observed in realkalisation tests using an electrical field of 830 V/m in carbonated concrete, while this effect was not noticeable in uncarbonated concrete. The mechanism and the controlling factors in terms of practical characteristics of structures need further study.

The development of realkalisation in time during the treatment is schematically shown in Fig. 8.9. The figure on the left shows the extent of carbonation before treatment. The middle figure shows the presence of alkaline material after a short duration: around the reinforcement (due to electrolysis) and from the surface into the concrete (due to absorption, electro-osmosis and/or diffusion). The right-hand figure shows a more advanced state of realkalisation, where the alkaline zone around the steel has become continuous with that penetrating from the surface.



8.9 Development of realkalisation detected with pH indicator; *left*: untreated, *middle*: after a short treatment, *right*: after longer treatment.

8.7.2 End-point determination

Unlike CP with its permanent current supply, but similar to ECR, successful ER requires that the treatment achieves a protected situation that is durable without further intervention. Consequently, the most important questions are how long should ER be carried on for an acceptable result and how can the absence of corrosion for a longer period after finishing the treatment be obtained? At present, there is no consensus on possible answers.

One view is based on the fact that the amount of hydroxyl produced by electrolysis is proportional to the charge passed and probably also the amount of alkali (carbonate) that penetrates. It is assumed then that after about 200 A.h/m^2 has passed, a protected and durable situation is guaranteed. For safety reasons mentioned with ECR, the average (design) current density should be kept below a few A/m^2. Consequently, after about 8 days at 1 A/m^2 the treatment can be stopped. A more conservative approach is based on the fact that different concrete compositions seem to react differently on ER, both in terms of immediate realkalisation achieved and the durability of the protective effect (see below). This view states that tests must be carried out to demonstrate that the pH is increased to sufficiently high levels throughout the concrete and that the amount of alkali present must be sufficient to withstand subsequent recarbonation. Although this approach makes sense from a performance point of view, the question of test methods requires attention. Testing of the pH achieved after ER is most widely accepted, but in some cases even high pH values have shown not to be sufficient proof of durability. The following paragraphs discuss these topics in more detail.

Phenolphthalein is a widely used pH indicator for measuring carbonation depths in concrete, turning from colourless to pink as the pH rises over about 9. However, pH 9 may leave the steel in an unpassivated condition. Thymolphthalein has a colour change near pH 10 and thus appears more appropriate. To be visible on concrete, the solution used has to contain 1 % thymolphthalein in a 70 % ethanol solution (Pollet and Dieryck, 2000). Sergi and co-workers (Sergi et al., 1996) suggest using a two-stage method applied to cored samples taken from the concrete structures that have undergone realkalisation. It involves the use of acid–base indicators and galvanostatic polarisation to determine the effectiveness of realkalisation treatment.

The matter of end point determination is further complicated by the influence of the cement type. Realkalisation of concrete made with blast furnace slag cement seems much more difficult than realkalisation of concrete made with Portland cement (Hondel and Polder, 1998; Pollet, 1999). After 14 days of realkalisation (total charge = 336 A h/m^2 of steel surface), nearly total realkalisation was observed for Portland cement (CEM I 42.5) concrete, as shown by a change to the colour purple after spraying phenolphthalein. However, after 28 days of treatment (charge = 672 A h/m^2) of concrete made with blast furnace slag cement (CEM III/A 42.5), only a small pink ring around the rebar was observed after spraying phenolphthalein and similar effects were found with fly ash cement concrete. It appears that concrete made with slag cement or fly ash cement needs considerably more electrical charge than does Portland cement concrete before it has reached a high pH over a substantial part of the cross-section. Consequently, the treatment time is longer for structures made with slag or fly ash cements. From laboratory tests, (Hondel and Polder, 1998) it was recommended that a charge of 100 A.h/m^2 of concrete surface for Portland cement and 350 A.h/m^2 for slag cement concrete should be applied. Further work has shown that a higher amount of charge is needed with slag and fly ash cement for the corrosion protection to be durable (see below).

8.7.3 Durability

Electrochemical realkalisation has been applied for over 15 years, mainly to structures made with Portland cement concrete. Although well documented case studies are rare, those available show that the corrosion protection obtained is durable (Odden, 1994). Laboratory tests followed over several years support the durability of the effect on reinforcement corrosion, as long as sufficient electrical charge has been applied. Elsener and co-workers (Elsener et al., 1998) reported half-cell potential measurements made after six months and after more than one year on a test site. The potential field was homogeneous with values around –200 mV CSE, indicating good corrosion protection.

Pollet and Dieryck (2000) have studied the durability of realkalisation of concrete specimens made with different cement types and different realkalisation durations:

- By following the steel potential for two years after realkalisation.
- By measuring the extent of the highly alkaline zone with a pH indicator just after treatment and two years after treatment.

The two types of measurement indicate a reduction of the effect of realkalisation with time. In the case of specimens made with blast-furnace cement (CEM III/A 42.5) and fly-ash cement (CEM II/A-M 42.5), this reduction leads to reactivation of corrosion. At the end of the realkalisation treatment, first potentials are very negative; then they change to rather positive values. In the case of blast-furnace cement and fly-ash cement, a subsequent change back to more negative values was observed with time, indicating a higher probability of corrosion. Visual examination of rebars two years after the treatment and the decrease of pH observed using indicators corroborate the potential measurements.

Summarising, it appears that realkalisation is able to achieve a high pH around the steel and throughout the concrete, reinstating steel passivation. It is unclear, however, how the treatment time should be determined, both in the design stage and then during treatment, in order to obtain a durable effect, in particular for concrete made with blended cements.

8.8 Advantages and limitations of electrochemical methods: prestressed structures

One of the main advantages of electrochemical methods is that they require only the removal of spalled and delaminated concrete, while mechanically sound but chloride-contaminated or carbonated concrete may be left in place. Consequently, less material has to be removed in comparison with conventional repair, causing less noise and dust to be produced and possibly resulting in shorter execution times. Because less of the cross-section needs to be removed, temporary structural support during concrete removal and repair, needed with conventional repair in special cases, may not be necessary with electrochemical methods. The other advantage is that they systematically take away the cause of the corrosion, because the current will find its path throughout the whole area to be treated. In contrast, taking away the corrosive factors by concrete removal and subsequent conventional repair *only* works in those areas where all the necessary steps are carried out to perfection, including removal of chloride ions from behind bars and inside corrosion pits. Consequently, the effect of electrochemical methods is more reliable and durable than the effect of conventional repairs.

Some of the limitations have been indicated above, such as the poor effect of ECR on corrosion due to mixed-in chloride. Limitations of CP are associated with durable adhesion of conductive coatings and overlays (shotcrete), which mainly depend on surface preparation prior to their application.

Another limitation may occur in the presence of prestressing steel. Strong polarisation of (stressed) high strength steel can have adverse effects related to hydrogen evolution according to Equation 8.2 and the risk of hydrogen embrittlement. As discussed above, with CP this can quite possibly be solved in most cases by carefully limiting the current density and monitoring the potential of the prestressing steel. For ECR and ER this is a serious problem. Due to the high current densities involved, the potential of the steel near to the anode is always depressed to hydrogen evolution potentials. It depends on the geometry of the structure (depth of rein-

Table 8.2 Cost indications for electrochemical maintenance methods, excluding concrete repair and access (COST 521, 2003)

Method	Cost in euro per square metre
Cathodic protection, conductive coating	100
Cathodic protection, titanium and overlay	200–300
Realkalisation	100
Chloride extraction	150

forcement, depth of prestressing steel, presence of isolating ducts, resistivity of concrete), whether ECR and ER are simply not possible in safety, or they may be possible taking safety factors into consideration, or they can be applied without serious risk. At present, specific tests are necessary on an individual case basis. It is hoped that these issues will be studied and solved on a more general level.

8.9 Economics

The cost of maintenance of concrete structures is a subject too complicated to be treated fully here. Many aspects related to the individual structure are involved, such as the amount of damage, the ease of access and the required surface finishing. From a survey among European experts some cost information was obtained (COST 521, 2003). It should be kept in mind, however, that national differences exist. Some methods are more popular in some countries, and some methods are almost absent in others. In Table 8.2, indicative costs of various electrochemical maintenance methods are given without including such items as cost of repair and scaffolding. The absolute level probably depends on the market situation in each country but the figures may serve for comparisons.

8.10 Sources of further information and advice

Various sources of further information exist, of which only a few can be mentioned. General information on these methods is provided in various documents supplied by international organisations and collaborative research, such as RILEM (Schiessl, 1994), COST 509 (1997), European Federation of Corrosion (Mietz 1998) and COST 521 (2003) and books such as those by Broomfield (1997). The number of internet sources of relevant information is increasing; see for instance CPA 1999–2001.

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