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Corrosion protection of reinforcing steels

technical report

Corrosion protection of reinforcing steels

Technical report prepared by

Task Group 9.7

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Cover image: Cracking of concrete due to reinforcement corrosion.

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Foreword

It has long been recognised that corrosion of steel is extremely costly and affects many industry sectors, including concrete construction. The cost of corrosion of steel reinforcement within concrete is estimated at many billions of dollars worldwide.

The corrosion of steel reinforcement represents a deterioration of the steel which in turn detrimentally affects its performance and therefore that of the concrete element within which it has been cast. There has been a great amount of work undertaken over the years in relation to the prevention of corrosion of steel, including the application of coatings, which has included the study of the process of corrosion itself, the properties of reinforcing steels and their resistance to corrosion as well as the design of structures and the construction process.

The object of this report is to provide readers with an appreciation of the principles of corrosion of reinforcing steel embedded in concrete and to describe the behaviour of particular steels and their coatings as used to combat the effects of such corrosion. These include:

- galvanised reinforcement,
- epoxy coated reinforcement,
- stainless reinforcing steel.

The report also provides some information on the relative costs of the materials and products which it covers.

It does not deal with structure design or the process of construction or with the post-construction phase of structure management including repair. It is hoped that it will however increase the understanding of readers in the process of corrosion of reinforcing steels and the ability of key materials and processes to reduce its harmful effects.

fib Commission 9 and its Task Group 9.7 wish to extend their gratitude to the creators of this report, Ulf Nurnberger and Hans-Wolf Reinhardt of the Institute of Construction Materials at the University of Stuttgart, and to those in Task Group 9.7 who helped with the review and editing.

Ben Bowsher
Convenor of Task Group 9.7

Contents

1 Introduction

In reinforced concrete structures the concrete guarantees chemical and physical corrosion protection of the unalloyed reinforcement. Thus, the alkaline electrolyte in the pores of the concrete passivates the steel and prevents anodic dissolution of iron. Further the concrete – as a more or less dense (fine porous) material - keeps corrosion-promoting substances away from the reinforcement. That is, if a sufficient depth of concrete cover and a high concrete quality are provided. In general, steel, in concrete is adequately protected against corrosion.

Loss of durability in reinforced concrete apart from problems caused by poor design and construction only occurs if the passivating oxide layer is rendered unstable (if depassivation occurs) due to carbonation of the concrete reducing the alkalinity of the pore solution in the hardened cement paste around the steel or to the ingress of chlorides to the steel /concrete interface [1,2]. Alkalinity can be lost by the ingress of carbon dioxide from the atmosphere into the permeable concrete, to neutralise the alkaline hydroxides by forming carbonates, thus lowering the pH. If the penetration front, which may also include moisture and oxygen reaches the reinforcement, corrosion may occur. The probability of this event depends upon the degree of permeability and porosity of the concrete.

Excessive chloride levels may arise from a number of sources, such as marine environments and the use of de-icing salts, particularly on roads, bridges and in car parks. Chloride ions together with water may penetrate into hardened concrete of structures. If the chloride content reaches a critical level at the surface of the reinforcement, the protective layer may be broken locally and pitting corrosion can take place. For non-carbonated concrete exposed to the atmosphere the critical chloride content is about 0,4 -1% by mass of cement.

As a result of the corrosion reaction rust forms and occupies a volume greater than that of the original metal. This process can cause cracking and spalling of the concrete, leading to further corrosion and a loss of bond between the concrete and the steel. A dangerous situation can then arise when a structural member loses cross-sectional area since there will then be increasing stress on the remaining section which could possibly lead to structural failure.

There are several conventional options open to the designer when long life is required or corrosion is anticipated. The most important corrosion prevention measures are good design, good site practice and quality control to resist carbonation and to exclude chlorides from any source. Contributory factors to these requirements are in particular details such as good mix design of concrete (minimal water/cement ratio, high cement content, using great care with any additives and adequate compaction as well as correctly curing) and concrete cover suitable for the corrosivity of environment [1,3,4]. In many cases this will provide sufficient corrosion protection for the embedded steel.

However environmental effects often are beyond design control. The ingress of moisture, air and salts due to service conditions in combination with inadequate design or incorrect site practice can defeat the best-laid plans. In these circumstances in which it is difficult to achieve the specified design life additional corrosion protection methods are needed. These methods include [1]:

- the impregnation of concrete with materials intended to reduce its permeability for carbon dioxide and water,

- the use of membrane-type products applied to the surface of concrete to limit chloride ingress into the concrete,

- the addition of corrosion inhibitors to the fresh concrete [5],

- the application of electrochemical techniques, such as cathodic protection or chloride removal [2,6],

- the use of corrosion protected reinforcement (galvanized and epoxy coated reinforcement) [2,7,8],

- the use of reinforcement made from stainless steel [9-14].

All these methods have a place as design alternatives and some are now standard practice. They offer a number of advantages over black steel, including an increased time to initiation of steel corrosion, a reduced risk of cracking and spalling of the concrete, an increase in service life of the structure and a reduction in the frequency and extent of repairs.

Corrosion protected or corrosion resistant materials for reinforcement may be used in the following applications:

- structures which are exposed to attack of corrosion promoting substances,

- where 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),

- where 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),

- in prefabricated wall- and roof-elements where the reinforcement connects the outer and inner walls,

- where non-dense or dense lightweight concrete is designed to reach a required thermal insulation as well as low own weight,

- in cases where access to the structure is strongly limited, making future inspection and maintenance costly, such as in underground structures in aggressive soil,

- where 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.

Coating material, which may be metallic or non-metallic, provides a barrier-type protection to the steel by isolating it from the local environment. Active metal coatings such as zinc coatings, provide not only barrier protection but also additional cathodic protection in special situations.

The use of hot dip galvanized coatings to provide additional protection to steel is most beneficial in chloride free concrete where carbonation has reached the level of reinforcement. Galvanizing may be recommended e.g. for reinforcements in precast elements, in lightweight concrete structures and in structures in contact with industrial atmospheres. Galvanizing also appears to provide an effective benefit when used in concrete containing chlorides in low or moderate concentration, e.g. in coastal constructions less than 1 km from the beach and in the spray zone of traffic structures.

Of all the organic coating systems available the most common is fusion bond epoxy coating. Experience concerning epoxy-coated reinforcement suggests that epoxy-resin coatings are able to provide long-term corrosion protection in chloride-contaminated concrete. However, a whole range of conditions must be adequately met to maximize the performance gains in relation to uncoated reinforcement. These chiefly include proper substrate preparation, including chromating, an adequate and uniform film thickness, the absence of pores and defects in the coating and careful steel fixing and concrete placing in order to prevent damage.

Stainless steel reinforcement, which is proposed and used for new reinforced concrete structures and for repair and modifications of existing structures, may be an economical and technically attractive approach. This material available in different alloy compositions has been undergoing development with the result that today it can claim to offer a total solution for providing corrosion-free concrete structures. Although the initial cost of stainless steel is much higher than that of carbon steel, its use can be justified on the basis that the increase in total project cost is small and is easily overtaken by the benefits of lower maintenance and repair costs, particularly where disruption times and costs for such work are taken into consideration.

Recommendations for a convenient use of stainless steel reinforcement are available [10,14-16]. The decision on which type of stainless steels to use depends on the degree of corrosion protection required, cost aspects, workability and required characteristics such as mechanical and physical properties and also weldability.

Typical applications where reductions in maintenance costs warrant the use of ferritic-austenitic and austenitic stainless steels include offshore structures, piers at the sea coast, parts of highway structures subject to de-icing salts or splash, multi-storey car parks, plants for the desalination of sea-water, concrete elements in thermal bath and various kinds of repair work. Guidance on locations where use of stainless steel reinforcement is recommended in new highway structures is published in [16]. It is possible to substitute all carbon steel reinforcement on a structure with corrosion resistant reinforcement but this would nearly always be too expensive to justify. Replacement with stainless steel reinforcement should be limited to those major components where the consequences of future repair are likely to be highly disruptive and costly and the possibility of chloride attack is likely.

The applications of stainless steels must not be restricted to chromium-nickel-(molybdenum) steels with austenitic and ferritic-austenitic structures. Ferritic chromium-alloyed steels might be the best choice in moderate aggressive environments, e.g. in carbonated normal and lightweight concrete if chloride attack can be excluded, where the higher resistance of the more expensive stainless steels is not necessary.

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2 Corrosion protection by concrete

2.1 Corrosion-protection capacity of concrete

2.1.1 Cement hydratation

Hardened concrete is an inorganic composite which consists of the binder and the mineral aggregates. The constituents of the binder are cement and Type I [1] additions like limestone or quartz powder and Type II additions which may be puzzolanic like fly ash, phonolite or trass or maybe latent hydraulic like ground granulated blast furnace slag or silica fume. In the fresh state, water is added to the concrete components in order to make the mix workable, and to start the hydration reaction of the binder. Every cement is a mixture of Portland cement clinker and other mineral materials. For the understanding of the corrosion-protection capacity of concrete, it is necessary to focus first on the hydration process of the clinker. Clinker consists of tricalcium silicate $3CaO{\cdot}SiO_2$, dicalcium silicate $2CaO{\cdot}SiO_2$, tricalcium aluminate $3CaO{\cdot}Al_2O_3$ and tetracalcium aluminoferrite $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$. Besides these main compounds, there are oxides of the alkalis sodium (Na) and potassium (K), there is a small percentage of MgO and free CaO, and there is SO_3 for set control. An average composition of Portland cement is given in Table 2.1.

Table 2.1: Average composition of Portland cement [2]

oxides	**range in mass-%**[1]
CaO	60 - 67
SiO_2	17 - 25
Al_2O_3	3 - 8
Fe_2O_3	0.5 - 6
$Na_2O + K_2O$	0.2 - 1.3
MgO	0.1 - 4
free CaO	0 - 2
SO_3	1 - 3

The clinker reacts with water to form hydrates, so that the water is chemically bound. The silicates convert to calcium silicate hydrate, the aluminates to calcium aluminate hydrate and ferrite hydrate, and which is very importantly, calcium hydroxide forms. The reaction equations are given in Table 2.2.

The first two lines show the production of calcium hydroxide, which is partly consumed by the hydration of the aluminates. Nevertheless, the total amount of $Ca(OH)_2$ produced from Portland cement clinker after full hydration is about 24 mass-%. Ettringite is later converted to monosulphate ($C_3A{\cdot}C\overline{S}{\cdot}H_{16}$). The alkali oxides, together with water form alkali hydroxides NaOH and KOH. The unhydrated cement combines with about 25% of its own weight of water.

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[1] mass-% - that is equal to the expression % by mass

Table 2.2: Reactive equations of clinker with water [2]

$$2\ C_3S^{1)} + 6\ H \rightarrow C_2S_2H_3 + 3\ CH$$

$$2\ C_2S + 4\ H \rightarrow C_3S_2H_3 + CH$$

$$C_3A + CH + 12H \rightarrow C_4A\ H_{12}$$

$$C_4AF + 2\ CH + 11\ H \rightarrow C_4AF\ H_{11}$$

$$C_3A + 3\ C\ \bar{S}\ H_2 + 26\ H \rightarrow C_3A{\cdot}3\ C\ \bar{S}{\cdot}H_{32} \qquad \text{“Ettringite”}$$

1) Short notation: $CaO = C$, $SiO_2 = S$, $Al_2O_3 = A$, $F_2O_3 = F$, $H_2O = H$, $SO_3 = \bar{S}$

Cement components other than Portland cement clinker and cement replacement materials react in a different way, puzzolanic material combines with calcium hydroxide from clinker hydration and latent-hydraulic material needs an activating agent, which is also the $Ca(OH)_2$, in order to hydrate. The composition of cement replacement material is shown in Table 2.3.

Table 2.3: Typical oxide compositions of cement replacement materials [3], in mass-%

oxide	**FA 1)**		**GGBS**	**SF**
	low lime	high lime		
SiO_2	48	40	36	97
Al_2O_3	27	18	9	2
Fe_2O_3	9	8	1	0.1
MgO	2	4	11	0.1
CaO	3	20	40	-
Na_2O	1	-	-	-
K_2O	4	-	-	-

1) FA = fly ash, GGBS = ground granulated blast furnace slag, SF = silica fume

Investigations of the calcium hydroxide content of hydrated Portland cement together with 25% fly ash, have shown that the $Ca(OH)_2$ content drops from 24% of pure Portland cement to 16% for the blend. If 50% GGBS is used, the $Ca(OH)_2$ is 9% without fly ash and 7% with fly ash. These values hold for a hydration duration of 365 days [4]. Silica fume consumes about twice as much as does fly ash. For this, reason the replacement content is limited to 11% in DIN 1045-2 [5]. Despite the lower $Ca(OH)_2$ content of the binder blends, the alkalinity is high enough for corrosion protection of the reinforcement.

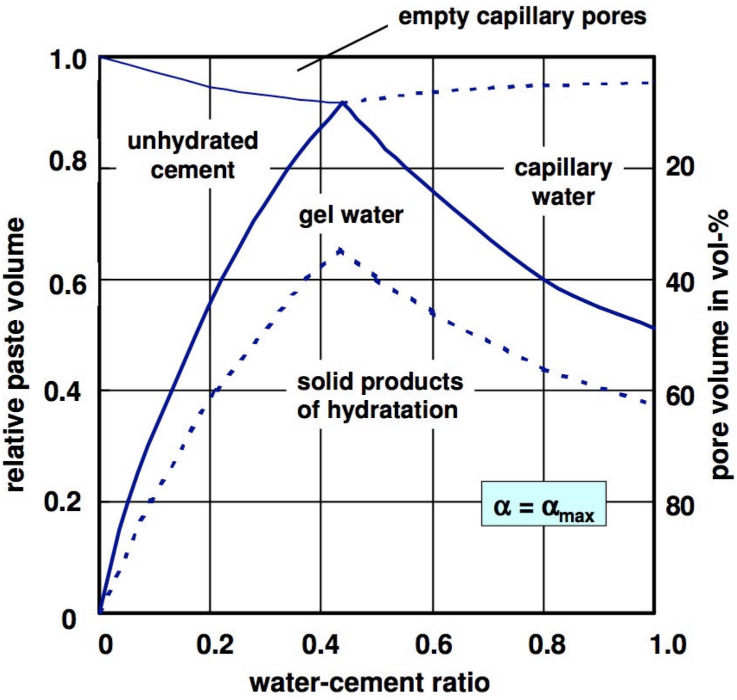

Fig. 2.1: Composition of hydrated cement paste and the final stage of hydration [6]
α = degree of hydration

2.1.2 Formation of pores

According to Table 2.2 new crystals form during hydration. The hydration products occupy a space about 1.8 times that of the unhydrated cement. The hydration will stop if the total space available is too small, which happens at very low water/cement ratio, or alternatively when the cement has totally reacted. There is a unique water/cement ratio at which the hydration products of 100% hydration exactly fit into the available space. This has been calculated to be 0.38 [6]. But this case only happens with prolonged storage in water. In reality there is either a shortage of water for complete hydration or a surplus of original space available due to high water/cement ratios. The results are capillary pores in the hydrated cement paste. Fig. 2.1 shows the volume partition in the final stage of hydration in sealed condition, i.e. there is no gain or loss of water. It can be seen that the amount of capillaries increases enormously with increasing water/cement ratio.

The capillaries are responsible for the transport of gases and fluids in the concrete, which is essential for corrosion of reinforcing steel. The hydrated cement paste is porous. These so-called gel pores are in the nanometer scale, and not important for transport mechanisms. At room temperature they are filled with water which is physically bound in some molecular layers on the very large internal surface of the hydration products (about 200 m^2/g).

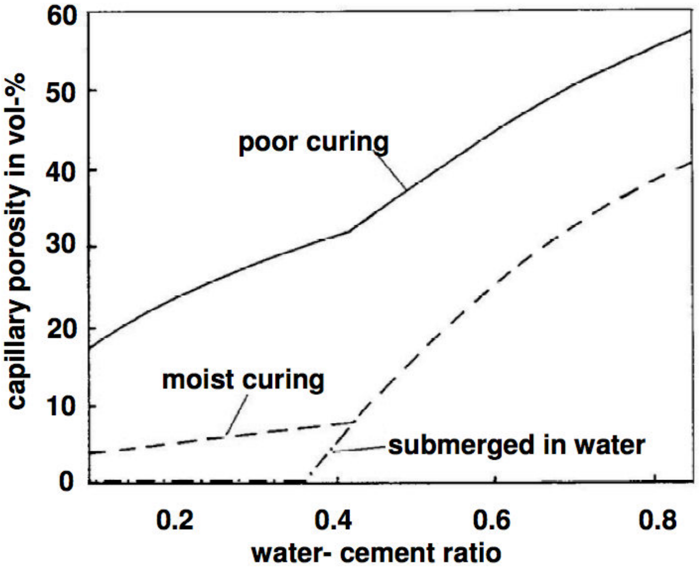

Fig. 2.2: Composition of hydrated cement paste at partial hydration

If the hydration stops due to shortage of water, i.e. if the concrete dries before the cement grains could completely hydrate more capillaries will form. This situation is shown in Fig. 2.2. Poor curing means that only 50% of the cement mass hydrated. This can happen if a freshly poured concrete surface is not protected and dries immediately.

The size of the pores is very different. Table 2.4 contains a classification of pores. To a great extent the micropores determine to a great extent the volume stability of the hydrated cement paste and hence of concrete, whereas the meso and macropores affect the mechanical strength and the transport properties. The water/cement ratio influences not only the total pore volume as shown in Figs. 2.1 and 2.2 but also the pore size. Fig. 2.3 gives an example of the pore size distribution in cement mortar, with water/cement ratios ranging between 0.40 and 0.75.

Table 2.4: Classification of pores [7]

designation	pore diameter	description
micropores	< 0.5 nm 0.5 - 2.5 nm	space for interlayer water in hydrated cement paste gel pores
mesopores	2.5 - 10 nm 10 - 50 nm	gel pores up to smallest capillary pores medium size capillary pores
macropores	50 nm - 10 µm	large capillary pores

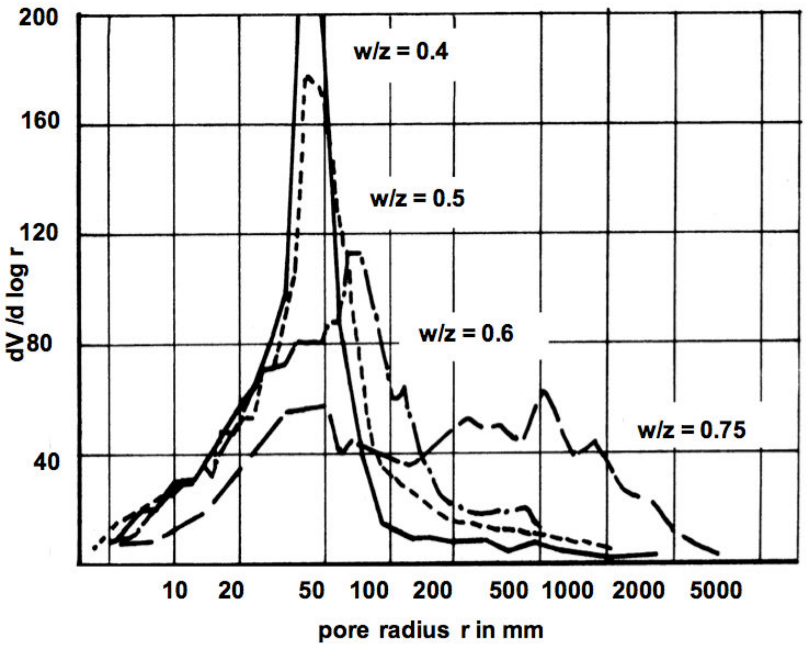

Fig. 2.3: Pore size distribution as a function of water/cement ratio [8]

The peak value of the distribution curve shifts to smaller pore sizes for lower water/cement ratios. This also means that the permeability decreases with lower water/cement ratio. There is always water in concrete. The larger pores may be partially filled with water, and the remaining space can contain water vapour which is in equilibrium with the ambient air. In the mesopores there is bulk water which can evaporate at low ambient humidity. The gel pores contain absorbed water due to the attractive surface forces. This water escapes only at a relative humidity which is lower than 30%. The interlayer water in the very fine pores can be removed only by strong drying. The chemically combined water is not lost on drying but decomposes only by heating to high temperatures in excess of 1000°C. Water in concrete is essential for corrosion of steel reinforcement, but can also be helpful for its protection.

2.1.3 Alkalinity of pore solution

Due to the solution of calcium hydroxide and alkali oxides, the pore water of fresh concrete has a pH of 13.0 to 13.8. This high alkalinity protects the steel from corrosion as has been illustrated by Pourbaix [9]. The diagram distinguishes from areas where corrosion takes place, when the metal is stable (immune) and when it is passivated.

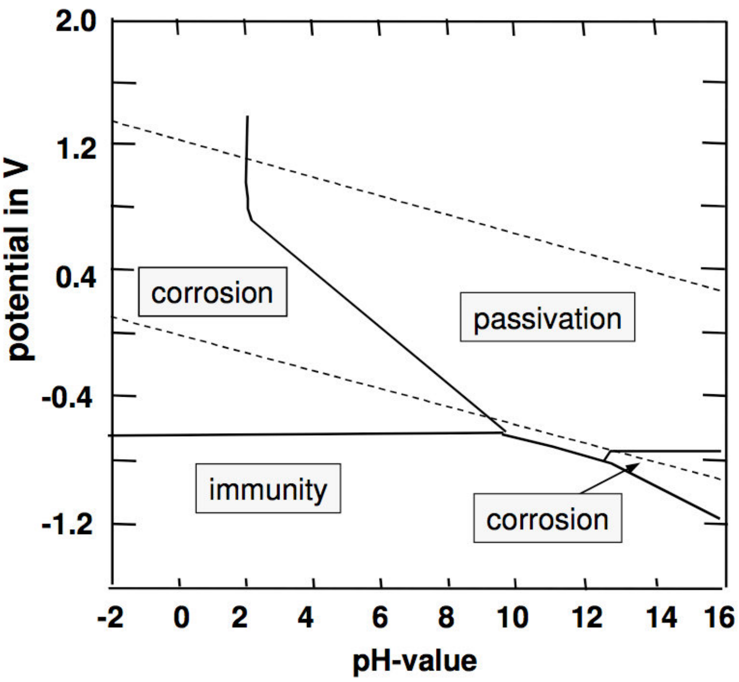

Fig. 2.4: Pourbaix diagram of iron in aqueous solution [9]

Passivation means that an iron oxide (Fe_3O_4) layer of about 50 nm is built up, which is non-conducting and protects the steel completely from corrosion. The pH of fresh concrete lies exactly in the window between the values of corrosion and stability. So it does not matter which potential difference there is the steel is either stable or passivated. It will be described later how the passivation layer can be destroyed.

2.1.4 Conditions for corrosion

There are always five preconditions to be fulfilled for corrosion:

- a potential difference on the steel is necessary,
- the steel must be electrically conductive,
- an electrolyte must surround the steel,
- oxygen must be at the steel surface,
- the passivation layer must be destroyed.

The first two preconditions are obvious, the last one will be discussed in the next chapter. The third and fourth will be discussed now. The electrolyte is the pore solution in the concrete. The pore solution contains ions of all kinds and is therefore electrically conductive. The conductivity depends on the moisture content of concrete and on the pore volume. The higher the moisture content and the larger the porosity, the more conductive the concrete. Table 2.5 shows gives average values for the specific electrical resistance of concrete.

Table 2.5: Specific electrical resistance of concrete in Ohm·m

water saturation	**water/cement ratio**		
	0.42	0.50	0.70
100%	80	40	20
80%		90	
60%		400	
40%	450000	90000	10000

It is clear that the resistance varies in a very great range. According to Faraday´s law, the corrosion rate is proportional to the current density. The current density is potential difference divided by the resistance and, thus, the resistance of concrete plays an important role.

The oxygen diffusivity in concrete is also strongly dependant on the water content and also on the pore space in the concrete. Fig. 2.5 shows an example. All lines have the same characteristic feature.

2.2 Reasons of reinforcement corrosion

2.2.1 Carbonation

There are two main reasons for the destruction of the passivation layer on the steel bar ("depassivation"): carbonation and chlorides. Carbonation takes place when the carbon dioxide of the air enters the concrete and reacts with alkali hydroxide and calcium hydroxide. The last reaction is described by the equation:

$$CO_2 + Ca\,(OH)_2 \rightarrow Ca\,CO_3 + H_2O$$

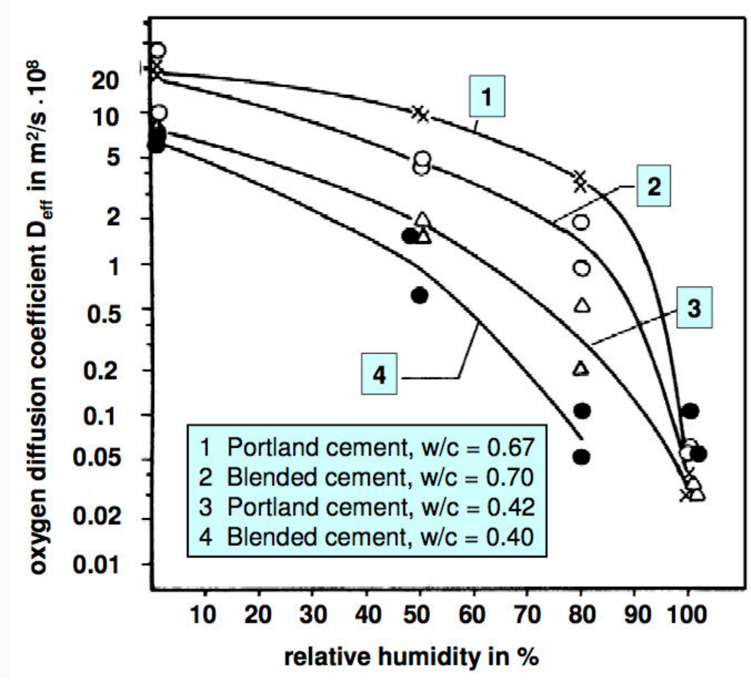

Fig. 2.5: Effective oxygen diffusion coefficient of Portland cement and slag cement concrete [10]

This reaction usually begins, and proceeds, if a certain amount of water is available. The carbonation front propagates as a function of the diffusivity of concrete, the carbonizable substances and time. The stationary diffusion equation (Fick´s 1st law), taking account of the chemical reaction which is fast compared to the diffusion transport, leads to the following expression:

$$x_c = \left(\frac{2 D c_0}{m_0} t \right)^{1/2}$$

with D = effective diffusion coefficient, c_0 = CO_2-content in the ambient air, m_0 = mass of CO_2 which can be combined with cement and t = time. The CO_2 content of the air can be taken as a constant as 0.03 mass-% or 0.6 g/m^3 air in normal environment. The other two quantities depend strongly on the concrete. The quantity of c0 is influenced by the type of cement. It is at its greatest with Portland cement and its smallest with slag cement. The carbonation depth increases in the following order when the same curing time is considered: Portland cement, Portland slag cement, portland puzzolan cement, slag cement. The carbonation depth of slag cement is about 60% more than Portland cement, with the same water/cement ratio. However, when slag cement is moist cured for a long period the carbonation depth is in the same order of magnitude. When the carbonation depth of a concrete with water/cement ratio of 0.42 is one, it is three for a water/cement ratio of 0.80. When concrete is not cured properly the skin of a concrete structure remains very porous and the diffusion coefficient is high. The carbonation depth is also strongly dependant on the moisture content. The diffusion coefficient is about 1.5 x 10^{-8} m^2/s in air and 0.8 to 5 $\cdot 10^{-12}$ m^2/s in water [11]. If a concrete gets wet and dry there is no carbonation during the period of water saturation. Fig. 2.6 shows the result of carbonation experiments, with clear distinction between dry and moist environments. In a dry climate, e.g. Spain, the carbonation proceeds quicker than in a rainy environment, e.g. Ireland.

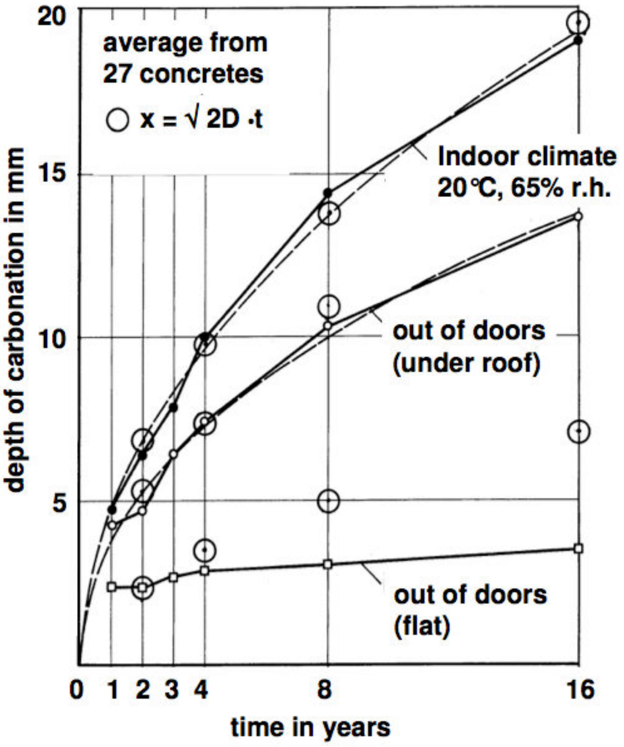

Fig. 2.6: Carbonation depth as function of time and environment [12]

Carbonated concrete has a pH value of the pore solution of less than 9, i.e. the portlantion does not occur anymore and the steel can corrode if the other preconditions are given (electrolyte and oxygen supply).

2.2.2 Chloride ingress

Chlorides are either chemically bound in the hydrated cement paste or free. The bound chloride amounts to about 0.4% of the mass of cement. However, in carbonated concrete this number drops to almost zero. The free chlorides in the pore solution can penetrate the passivation layer and cause corrosion. This can be explained by Fig. 2.7.

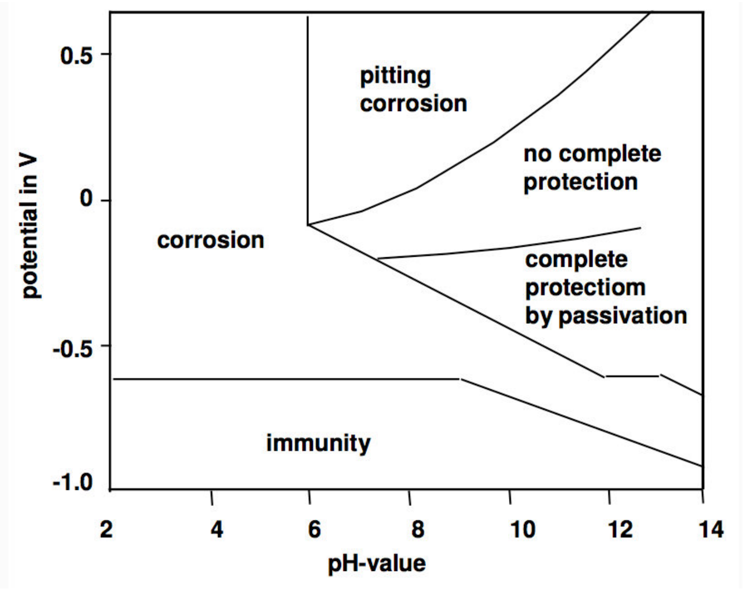

Fig. 2.7: Pourbaix diagram for iron in chloride solution [9]

As opposed to that shown in Fig. 2.4, there is no region where the steel is immune or passivated independently of the potential difference. Between the regions of the pH of virgin concrete (pH = 13) and that of carbonated concrete (pH = 9) there is always a region with corrosion and since the potential difference is not predictable one must assume that corrosion can take place. At high potentials, there is a risk of pitting corrosion, even in a non-carbonated concrete. The starting point for pitting corrosion is a high chloride concentration and a OH^-/Cl^- ratio according to the following equation from [13].

$$\log c_{cl,crit} = 1.5 \log c_{OH} - 0.245$$

with $c_{cl,crit}$ = chloride ion concentration, where pitting corrosion is probable, and c_{OH} = hydroxide ion concentration.

The question may be asked: how do the chlorides enter the concrete? Firstly, one has to consider the source of chlorides. This can be seawater, de-icing salts, production facilities of chlorides, usage of chlorides like in bleaching installations, or fire where PVC is involved. One must also consider the transport into concrete. This can be diffusion, capillary suction or permeation. Diffusion takes place in the saturated state of concrete where chloride can diffuse in the pore solution.

The governing equation reads:

$$x_{Cl} = \left(D_{Cl} t\right)^{1/2}$$

with x_{Cl} = depth of chloride front for a constant chloride concentration, D_{Cl} = effective diffusion coefficient, i.e. the binding capacity is already considered, and t = time. The diffusion coefficient ranges between 0.5 and 20 · 10^{-12} m^2/s [14]. A very effective transport mechanism is capillary transport, especially in combination with the alternating conditions of wetting and drying. The governing equation reads:

$$x_{cap} = B\, t^{1/2}$$

where x_{cap} = depth of capillary front, B = penetration coefficient and t = time. The penetration coefficient ranges between 0.05 and 0.15 · 10^{-3} m $s^{-1/2}$ [15]. Capillary transport together with drying, leads to an accumulation of salt.

The third transport mechanism is permeation which takes place with high water pressure. Whilst this may take place in deep-sea offshore installations, this transport does not play a role in normal structures. A good example of exposure tests in the North Sea is shown in Fig. 2.8. The left hand diagram refers to the exposure above high water, i.e. this is the zone with capillary suction and drying. The middle one belongs to the tide zone, i.e. there is less drying and almost saturation of concrete with diffusion as main process. The right hand diagram concerns the submersed zone with diffusion in saturated concrete. The differences of chloride in concrete is as expected from the mechanism as discussed above. The influence of water/cement ratio can be clearly seen, and the type of cement also has an effect which will be discussed in the following chapter.

Cracks in concrete may reduce the corrosion protection. If carbonation is involved, one can assume the following model. Carbon dioxide will penetrate through the crack and the pH of the pore solution will drop below the passivation level. The steel will start to corrode at the place of the crack. Corrosion stops when corrosion products and deposition of calcium carbonate block the crack and when, at the same time, calcium hydroxide is leached from the deeper zone of concrete and is transported to the corrosion spot. This mechanism, called realkalizing, delays the onset of corrosion as long as the concrete cover is not carbonized in total. This mechanism holds as long as the crack width at the surface of the concrete element is not larger than 0.40 mm.

Cracks in chloride-affected concrete are always a danger, because there is no minimum crack width without corrosion risk. Even a crack width of 0.10 mm can be dangerous if the chloride stays in the crack, e.g. in a horizontal slab of a car park, and reaches the steel. If the chloride is washed out from time to time it is not so dangerous. If the concrete is always immersed it is also not so risky, because of the lack of oxygen required for corrosion.

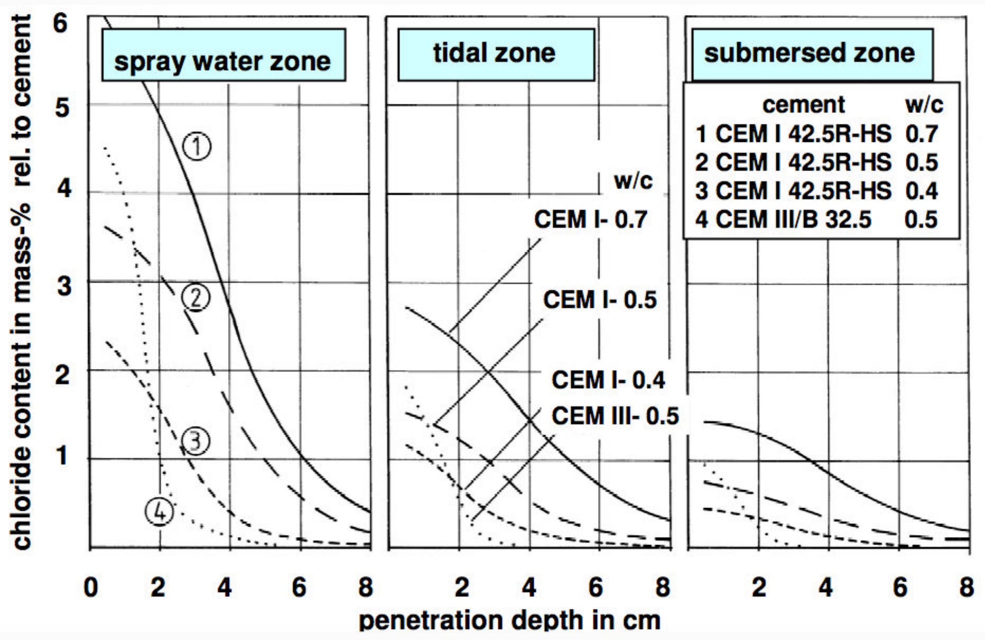

Fig. 2.8: Chloride concentration in various concretes [16]

2.3 Enhancement of corrosion protection

2.3.1 Water/cement ratio and type of binder

2.3.1.1 Concrete with Portland cement

The capillary pores in concrete determine the transport properties, i.e. diffusion of gases and ions, capillary suction of water and other fluids, and permeability of fluids and gases. As has been shown in Figs. 2.1 to 2.3, the water/cement ratio is the key parameter for the capillary porosity. Fig. 2.9 shows an example of capillary suction where the sorptivity (i.e. absorbed volume fluid per area and square root) is plotted vs. the water/cement for five fluids. For water, the increase in water/cement ratio of 0.40 to 0.70 amounts to a factor of eight.

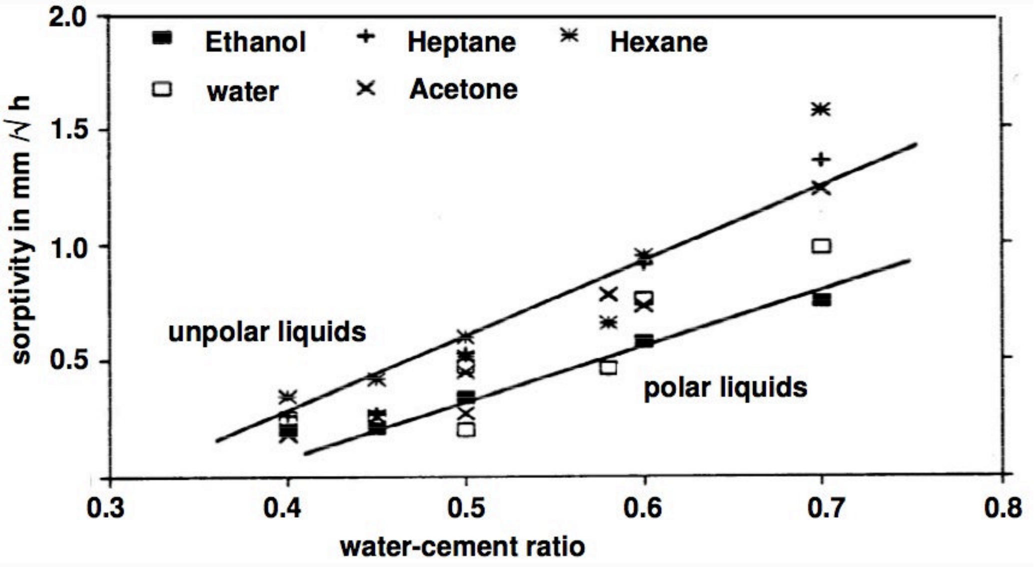

Fig. 2.9: Sorptivity vs. water/cement ratio for five fluids [15]

The strong influence of the water/cement ratio on water permeability is indicated by the following equation:

$$k = 2.8 \cdot 10^{-10} \left(\frac{w}{c} \right)^5$$

with k in [m/s] and w/c = water/cement ratio [17]. Also the diffusion coefficient depends strongly on the water/cement ratio as Fig. 2.10 shows. Despite the fact that the vapour of some organic fluids were investigated, the picture shows the increase of the diffusion coefficient by one to two orders of magnitude when the water/cement ratio rises from 0.40 to 0.70.

The oxygen diffusion coefficient has been measured on Portland cement concrete with water/cement ratio of 0.4, 0.6, and 0.8 and amounted to 0.75, 3.10, and $5.70 \cdot 10^{-9}$ m^2/s [18].

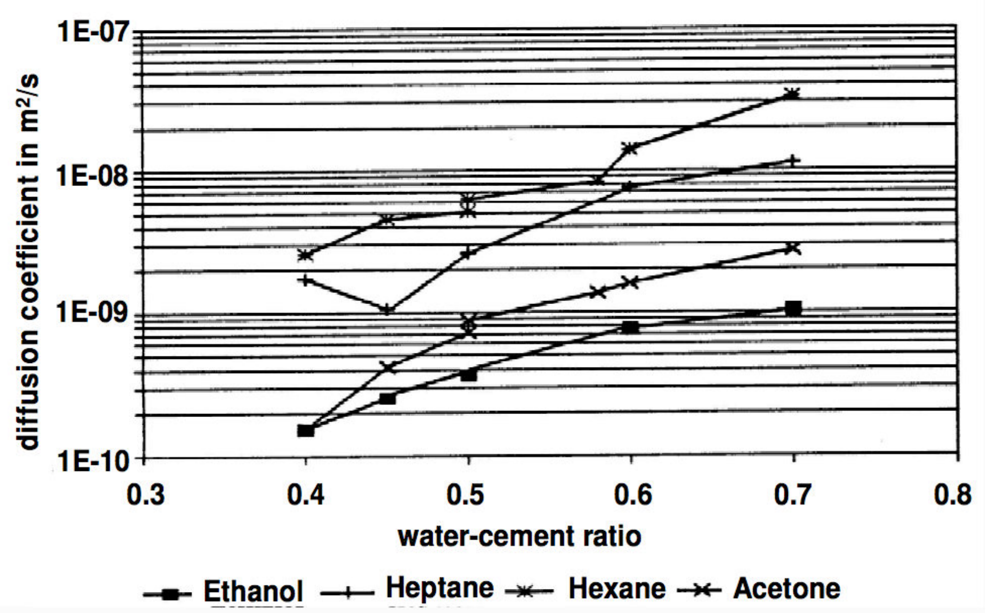

Fig. 2.10: Diffusion coefficient vs. water/cement ratio for four vapours [19]

2.3.1.2 Concrete with slag cement

The type of binder has a great effect on the transport properties. Slag cement leads to a slightly higher oxygen diffusion coefficient compared to Portland cement when cured for 7 days. The storage conditions play an important role due to the different water saturation of the small capillary pores. Storage at 95% relative humidity reduced the diffusion coefficient by almost two orders of magnitude compared to a storage at 65% relative humidity [18]. The most striking influence on chloride diffusion has been found for slag cement. Fig. 2.11 shows the influence of ground granulated blast furnace slag in cement on the diffusion coefficient of Na and Cl ions [20]. For quantities up to about 20% ground granulated blast furnace slag there is no influence, but higher contents of ground granulated blast furnace slag lead to a steep reduction of the diffusion coefficient. Another reference [21] contains algebraic expressions for the influence of ground granulated blast furnace slag on the diffusion coefficient.

The diffusion coefficient is given by

$$D = 85,7 \frac{Z_N}{P_N} \cdot 10^{-12} \ \frac{m^2}{s}$$

which is valid between -20 and +50°C. The parameter Z_N is temperature dependent, as shown in Table 2.6. The diffusion coefficient is obviously about 4 times at 50°C compared to 20°C and only about a tenth at -20°C.

Table 2.6: Temperature dependent parameter for diffusion coefficient [21]

temperature, °C	-20	-10	0	10	20	30	40	50
Z_N	0.11	0.20	0.36	0.61	1.00	1.58	2.43	3.67

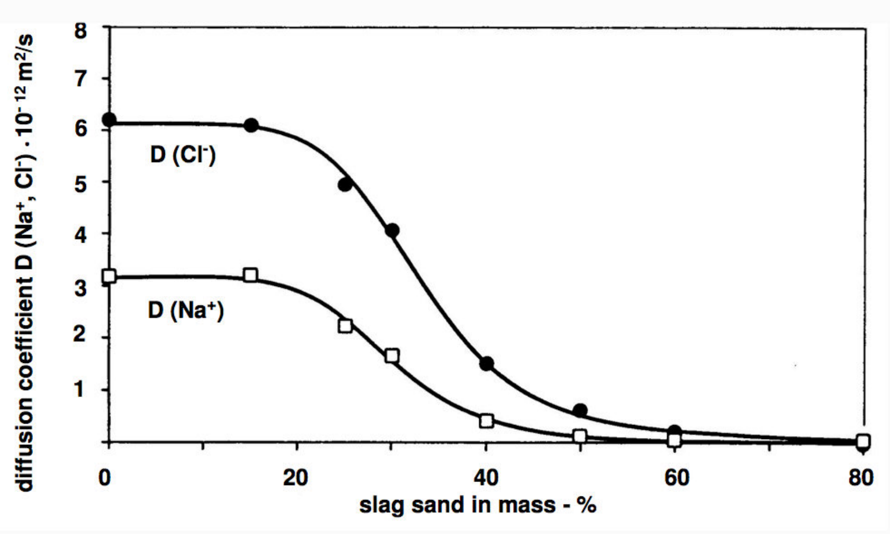

Fig. 2.11: Influence of ground granulated blast furnace slag on diffusion coefficient of sodium- and chloride-ions [20]

The parameter P_N is energy dependent and represents the number of positions which can react with chloride. P_N has been determined for various cements and additions, the reference [21] contains extensive tables from which only a selection is given in Table 2.7.

The numbers depend also on the water/cement ratio of the concrete. The table shows clearly that an increase of the water/cement ratio from 0.4 to 0.7 increases the diffusion coefficient by a factor of three, and that the addition of 70% ground granulated blast furnace slag reduces the diffusion coefficient by about a factor of 1000 for $w/c = 0.4$ and by about a factor of 18 for $w/c = 0.7$. The influence of the C_3A content is also evident. Fly ash has also a considerable influence as well as trass. The adverse effect of ground granulated blast furnace slag on chloride transport is not only the decrease of the diffusion coefficient but also the increase of the chloride binding [22].

2.3.1.3 Concrete with fly ash

The influence of fly ash on the chloride diffusion coefficient has been investigated recently [23]. Fig. 2.12 shows the chloride migration coefficient as function of age and fly ash content. Z1 represents Portland cement and F2 represents fly ash. One can clearly see that the addition of 20% fly ash reduces the migration coefficient by about 20 times and addition of 40% by about 30 times compared to Portland cement. It can also be seen that a hydration time of 28 days has practically no effect. The minimum time is 91 days and a longer time is always beneficial.

Table 2.7: Parameter P_N for diffusion coefficient [21]

type of cement	water/cement ratio			
	0.4	0.5	0.6	0.7
Portland cement 35 with 1% C_3A	14	12	9	5
Portland cement 35 with 7% C_3A	71	61	43	24
Portland cement 35 with 1% C_3A and 20% ggbs$^{1)}$	17	14	12	6
Portland cement 35 with 1% C_3A and 70% ggbs$^{1)}$	1714	1071	428	107
Portland cement 35 with 1% C_3A and 30% fly ash	66	48	32	19
Portland cement 35 with 1% C_3A and 30% trass	19	14	12	8

1) ground granulated blast furnace slag

If the migration coefficient drops, the electrolytic resistance increases as described in Fig. 2.13 shows. This holds for mixtures with fly ash or ground granulated blast furnace slag, as indicated by the shaded area. The addition of silica fume has a positive effect on the tightness of concrete by reducing the porosity and the size of the pores. Since silica fume is mainly used in high-performance concrete, the effect is discussed in the next chapter.

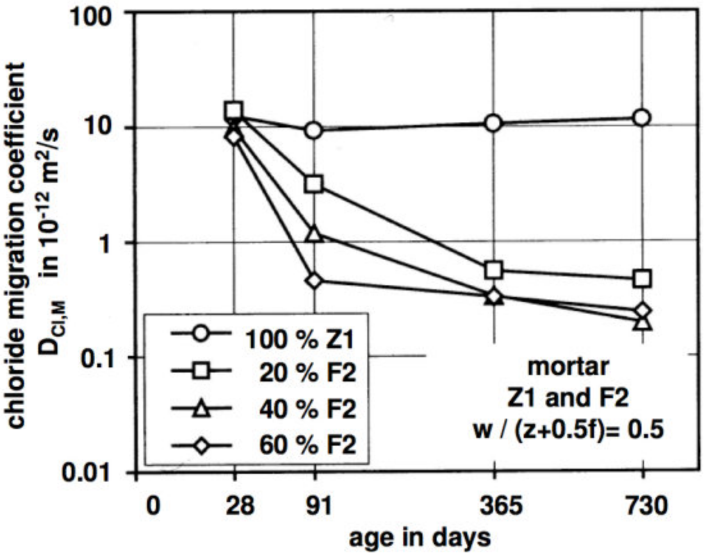

Fig. 2.12: Chloride migration coefficient as function of age and fly ash content [23]

In summary, it can be concluded that the pore system is narrowed by the addition of ground granulated blast furnace slag, fly ash, silica fume and trass which reduces the diffusivity up to the factor of 100 and increases the electrolytic resistance up to a factor of 100 simultaneously. A second conclusion is that the reduction of the water/cement ratio also helps and that a long curing time is important, especially if puzzolanic additions are used.

2.3.2 High-performance concrete

The term "high-performance" is mainly used in connection with "high-strength". The European standard EN 206 defines a concrete with a strength class higher than C50/60 as high-strength concrete. But apart from strength, high-performance includes other properties as well, such as very good workability, tightness against hazardous media, or good fire resistance, just to mention some. High-performance concrete is usually produced with a low water/cement ratio and, very often, with the portland of silica fume. The very important influence of a low water/cement ratio on the transport properties has already been discussed. In this chapter, the addition of silica fume shall be addressed.

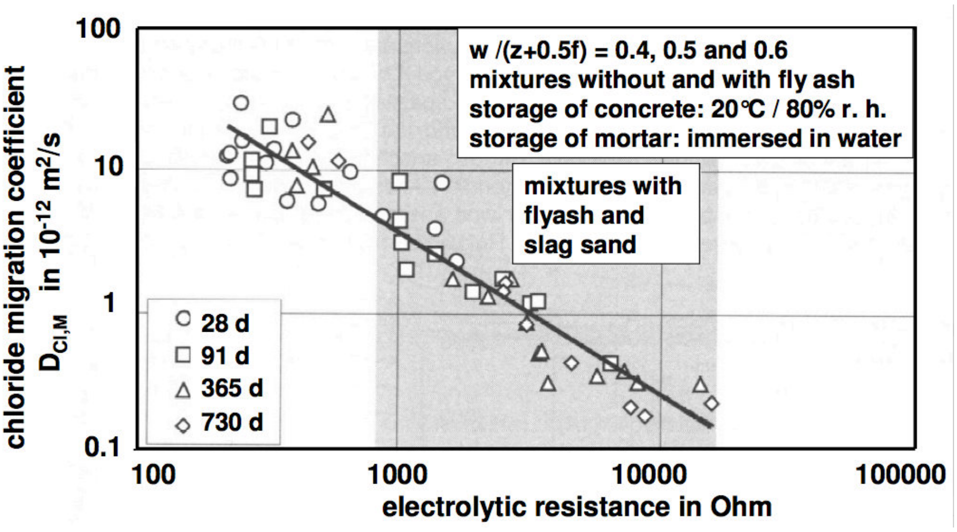

Fig. 2.13: Chloride migration coefficient vs. electrolytic resistance [23]

Silica fume is an extremely fine material with grain sizes smaller than 0.2 µm. It consists of amorphous silica which reacts with the $Ca(OH)_2$ which is produced during the hydration reaction of Portland cement klinker. Due to its fineness, the packing density of the binder gets larger. The effect of the packing density has been discussed in [24]. Concrete with silica fume and, at the same time, a low water/cement ratio can only be made with efficient plasticizing admixtures. A typical composition of a C100/115 is given in Table 2.8. Such a concrete possesses only a small amount of capillary pores and is therefore rather impervious. Fig. 2.14 shows an example of chloride distribution after 182 days of exposure in seawater.

Water permeability and water vapour diffusion has been investigated on high-strength concrete with water/cement ratios of 0.33 and 0.37 and 15% silica fume with respect to the cement content. The permeability ranged between 1.0 and $1.5 \cdot 10^{-14}$ m/s while the diffusion coefficient varied between 1.0 and $1.5 \cdot 10^{-7}$ m^2/s. These values were about 5 times lower than the values of concrete with a water/cement ratio of 0.45 [26].

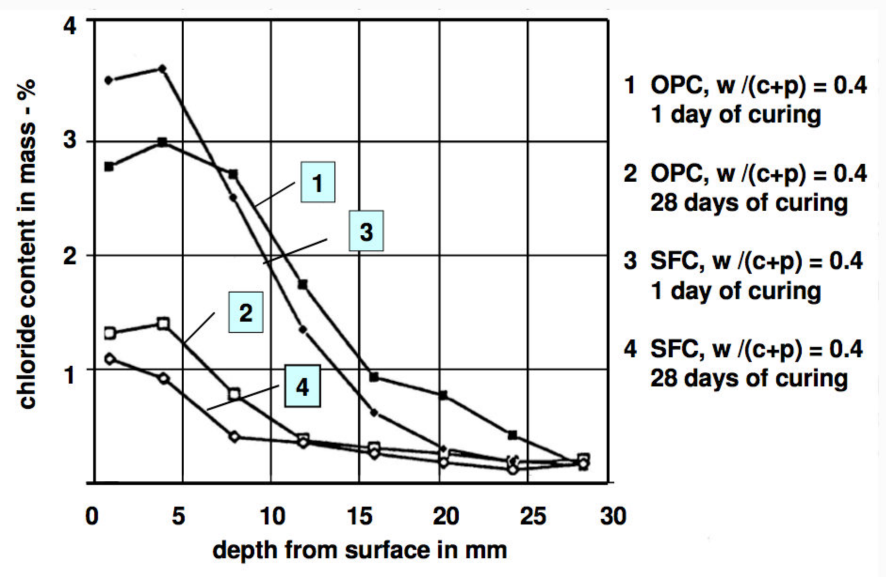

Fig. 2.14: Chloride distribution in concrete with and without silica fume [27]

A completely new generation of high-performance concrete is the ultra high performance concrete (UHPC) or reactive powder concrete, which provides transport properties which are some orders of magnitude smaller. This special concrete is still in development [28].

2.3.3 Self-compacting concrete (SCC)

Self-compacting concrete is a concrete which contains more fine material than conventional concrete. It can be characterized as a two-phase material, one phase being the paste and the other the aggregates. The cement paste is enriched by limestone powder, quartz powder, fly ash, plasticizer, viscosity agents and maybe retarder. There are three types of SCC: powder type, viscosity agent type and combination type. The viscosity agent type is the closest to conventional concrete, whereas the powder type needs about 35% paste by volume. The combination type is in between.

As corrosion protection is concerned, one has to assess the transport properties and the alkalinity. The alkalinity does not differ from conventional concrete, since the same cements and also about the same amount of cement are used. The transport properties are mainly dependent on the water/cement ratio (and thus the strength class) and the type of binder and, if they are equivalent to conventional concrete, the transport properties are not significantly different [26].

Table 2.8: Typical composition of high-strength concrete [25]

component	mass in kg/m^3
Portland cement CEM 52.5 R	450
silica fume	45
water	148
plasticizer	23
retarder	2
sand 0-2 mm	829
crushed aggregate 2 - 5 mm	270
5 - 8 mm	207
8 - 11 mm	353
11 - 16 mm	415
water[1)]/(cement + silica fume) ratio	0.33

[1)] The water of the plasticizer has been added with 65%

2.3.4 Controlled permeability formwork (CFP)

Controlled permeability formwork (CFP) systems generally consist of a combined filter and drain supported by conventional formwork [29]. Both are specially engineered fabrics (textiles). The product thickness is less than 2.5 mm. The fibre should have a pore size of less than 0.05 mm in order to retain the majority of cement fines while permitting the controlled removal of excess water from the concrete/formwork interface. A schematic of the effect of CFP is shown in Fig. 2.15.

As can be seen, the excess water is removed by gravity forces whilst the air moves upwards and escapes. The result is that the concrete cover zone of about 20 mm has a lower water content and, due to this, a lower water/cement ratio. The porosity in this zone drops and the cement content is a little higher than in the bulk concrete. Blowholes are avoided in the main. All aspects lead to an improved durability.

Tests on concrete with CFP showed a reduction of the chloride diffusion coefficient by 62% and a reduction of carbonation depth to zero after 3 months [30]. In another test series it was concluded that the chloride diffusion rate and chloride contamination at the cover depth gave a reduction by factors of approximately 2 and 3 against impermeable formwork [31].

As far as the corrosion of rebars is concerned, the CFP extended the time to the achievement of corrosion potentials by approximately 2 to 3 times [31]. Similar results were reported in [33]. Apparent chloride diffusion coefficients have been determined on concretes with water/binder ratios of 0.43. The average coefficient of the control concrete with portland composite cement (CEM II) was $25.6 \cdot 10^{12}$ m^2/s, whilst the concrete with CFP showed one of $16.7 \cdot 10^{-12}$ m^2/s [34].

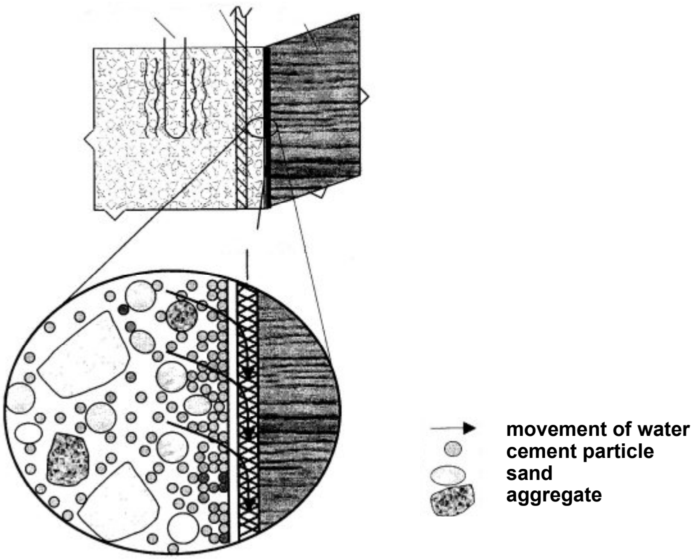

Fig. 2.15: Schematic of CFP effect [30]

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3 Galvanized steel reinforcement [1-6]

3.1 Manufacture of the coating [3,7]

Steel reinforcing bars can be protected by a coating applied by dipping appropriately prepared steel bars into a molten bath of zinc. In this hot dip galvanizing process, bars or welded cages, after pickling and dipping in an aqueous preflux solution of zinc ammonium chloride to increase the reactivity, are immersed in a bath of molten zinc at about 460 °C. When the steel bars are submerged in the zinc bath, the two metals react in some depth. After removal and cooling, the coating consists of several layers of iron-zinc alloys metallurgically linked to the base steel, and an external layer of nearly pure zinc. The sequence of layers from the steel substrate to the exterior surface of the coating is as follows (Fig. 3.1):

Gamma layer - very thin and usually not discernible; it has a cubic structure with 21 - 28 % Fe

Delta layer - usually consisting of two layers: an internal 'compact' and an exterior 'barrier'; the structure is hexagonal with 7 - 12 % Fe

Zeta layer - formed by very asymmetric monoclinic crystals with 5.8 - 6.8 % Fe; their presence diminishes the ductility of the coating

Eta layer - the external skin of almost pure zinc.

The thickness of these layers vary according to the composition of the steel, the temperature of the bath, the composition of the zinc bath, and the time of immersion [8]. When galvanized steels are heated above about 250°C, the growth of the Zeta layer is accelerated, which results in a consummation of the Eta layer at the surface. This effect is utilized in the manufacture of galvannealed products, with conversion of the coating fully to an iron-zinc alloy.

As to the steel composition, the silicon content is of the greatest influence. If this is either between 0.02 and 0.15 % (Sandelin effect) or greater than 0.25 %, the reactivity between steel and zinc is higher and the alloy layers may become considerably thicker (Fig. 3.2). Furthermore, coatings with a too high thickness and especially too high thickness of Zn-Fe intermetallic compounds are brittle and tend to crack and flake during bending of the bars. Since the steel of reinforcing bars often comes from the recycling of scrap-steel, it is practically impossible to find steel bars on the market with a silicon content less than 0.03 %. Therefore the best choice, with respect to the chemical analysis and not too thick coating, is to have a silicon percentage in the range 0.15 - 0.25.

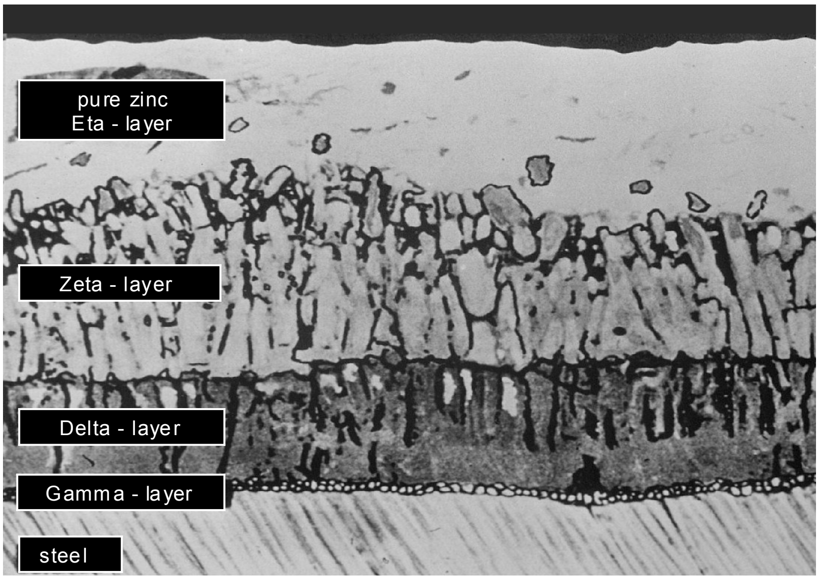


Fig. 3.1: *Structure of the coating of a hot dip galvanized steel*

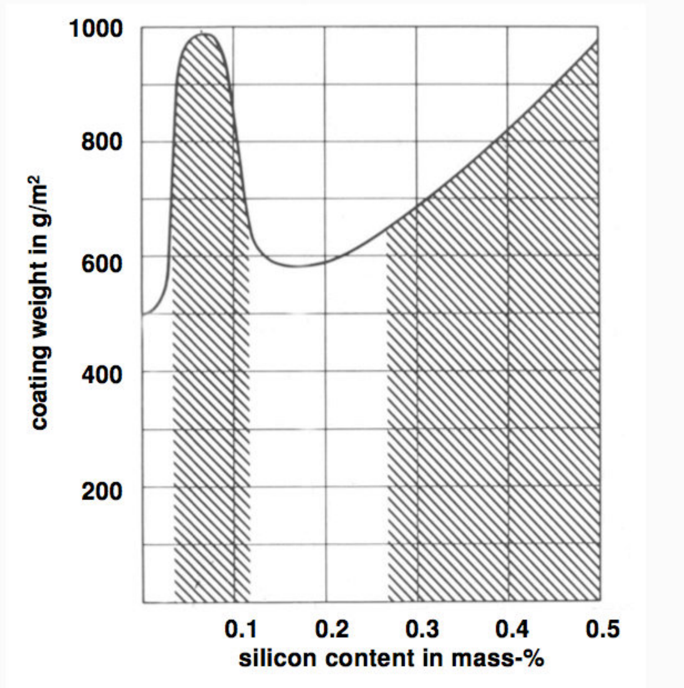


Fig. 3.2: *Influence of silicon content in steels on zinc deposition*

The time of immersion usually is between 1.5 and 5 minutes. In the first minute the thickness of the layers increase rapidly. Later the growth decreases and is finally very slow. The thickness of iron-zinc layers varies, depending on immersion time and silicon content. On the average the result is usually from 50 µm to about 300 µm.

The galvanized bars are withdrawn from the bath slowly and at a uniform rate to allow excess zinc to flow back into the bath. During withdrawal the bars are agitated and their underside scraped with skimmers to eliminate heavy drips and runs. Experience shows that ribbed bars of smaller diameters get thicker coatings of pure zinc [8]. Contributing factors are: firstly thin bars cool much faster, and secondly they have shorter distances between their ribs.

More pure zinc is then taken along from the bath. Fig. 3.3 shows the coating of ribbed bars in case of too thick Fe-Zn layer, too thick pure zinc layer and optimal coating. Ribbed bars of small diameter (diameter < 7 mm) get extra thick coating in the transition zone from the bar core to the ribs (Fig. 3.3, above).

Ribbed bars automatically receive an extra thick coating in the transition zone from the bar mantle to the ribs, especially for small diameter bars (see chapter 3.2.1). At normal stresses these transition zones represent critical areas, and when bending the strains are concentrated at these spots. Cracks in the layers must be expected. In thick layers even scaling may occur. The time of immersion should therefore be as short as possible, and zinc should be allowed to drip off during withdrawal from the bath.

As a last step, the reinforcing bars are often chromate treated by a quench into a water-chromate solution. The intention is to reduce any reaction between the alkaline cement paste in fresh concrete and the zinc surface during initial curing of the concrete (chapter 3.2.4). However, some researchers indicate that this process is unnecessary.

3.2 Properties of coating and of galvanized reinforcement [3,7]

3.2.1 Coating properties

After galvanizing the coating is composed of different iron-zinc layers and an external layer of pure zinc, as described (Fig. 3.1). The intermetallic compounds are very hard and brittle. Galvanizing results in a rather tough coating as the alloying layers show mostly larger hardness than the base steel. Typical results of hardness tests are:

layer:	**hardness:**
base steel	159 DPN
delta layer	244 DPN
zeta layer	179 DPN
eta layer	70 DPN

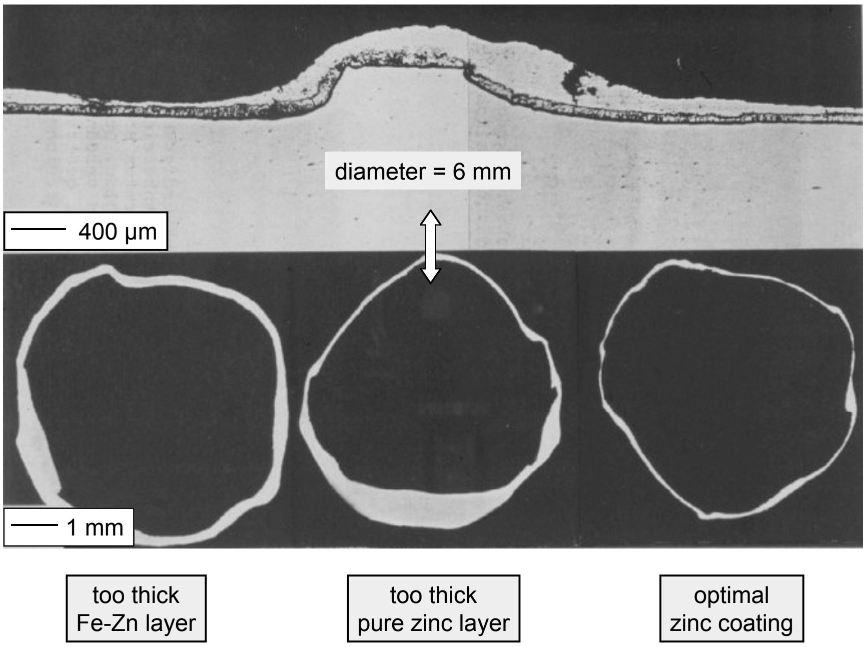
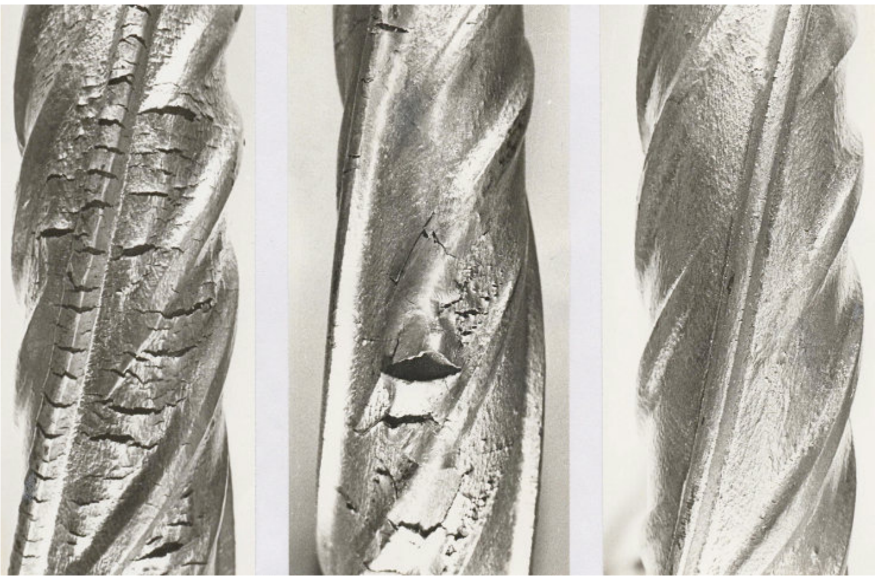


Fig. 3.3: Thick coating in the rib area of a small diameter reinforcing steel (DPN = Diamond Pyramid Number)

As a result, zinc coating has a very good abrasion-resistance, but its brittleness can affect the adherence and cracking of the coating when handling galvanized reinforcement.

One of the major concerns of engineers in using galvanized bars in reinforced concrete is the cracking of the zinc layer when bending and the consequent loss of adhesion of the coating to the substrate steel. The extent of cracking and the width of cracks are influenced by the bend radii, the diameter of the bars, the angle of bend and the thickness of the coating. In order to provide adequate adhesion, and to avoid cracking and flaking if impacted or bent on site, the thickness of the iron-zinc layers should not be exceed 80 to 120 µm. A maximum of insensitivity is guaranteed if the thickness of the sum of the iron-zinc layers is clearly below 80 µm.



Fe-Zn layer too thick | pure zinc layer too thick | optimal zinc coating

Fig. 3.4: Behaviour of coatings during bending around a smaller mandrel [8]

Cracks in the layers must be expected. Scaling may even occur when thicker layers are present. Fig. 3.4 shows the typical behaviour of galvanized steel with too thick a Fe-Zn layer and even thicker layers of pure zinc when bending around a smaller mandrel. To avoid wide cracks and flaking, the thickness of the zinc coating and above all the thickness of the iron-zinc alloy layers have to be limited [8]. The risk of wide cracks and flaking of zinc coating is lower if a suitable steel is used (see chapter 3.1) and correct galvanizing parameters are met. The time of immersion should therefore be as short as possible (about 1 minute), and zinc be allowed to drip off during withdrawal from the bath. The speed of withdrawal should be about 5 m/minute for bars of diameter 10 mm or less, and 10 m/minute for larger bars. Ribbed bars of smaller diameter in principle tend to receive thicker layers of pure zinc.

Also, a correct use of the mandrel for bending galvanized bars is important. Larger bar sizes require larger mandrels to ensure that the coating remains intact. Regarding the standards related to bending of galvanized steel bars, the minimum bend diameters of the mandrel can be taken from the national standards and codes for non-galvanized steel bars (D from 6d to 10d as bar size increases). However, many tests have shown, that bars in a corrosive environment showed no corrosion products at the cracks produced by bending.

There was also evidence that zinc oxide corrosion products had blocked the cracks in the coating thereby preventing localised corrosion of the base metal [9].

For practical and/or economical reasons, and to minimize the damaging effects of bending after galvanizing, bending may take place prior to galvanizing. Some standards, e.g. in Germany, forbid bending prior to galvanizing because of the risks that cold working of the microstructure of the steel could result in strain age embrittlement during galvanizing.

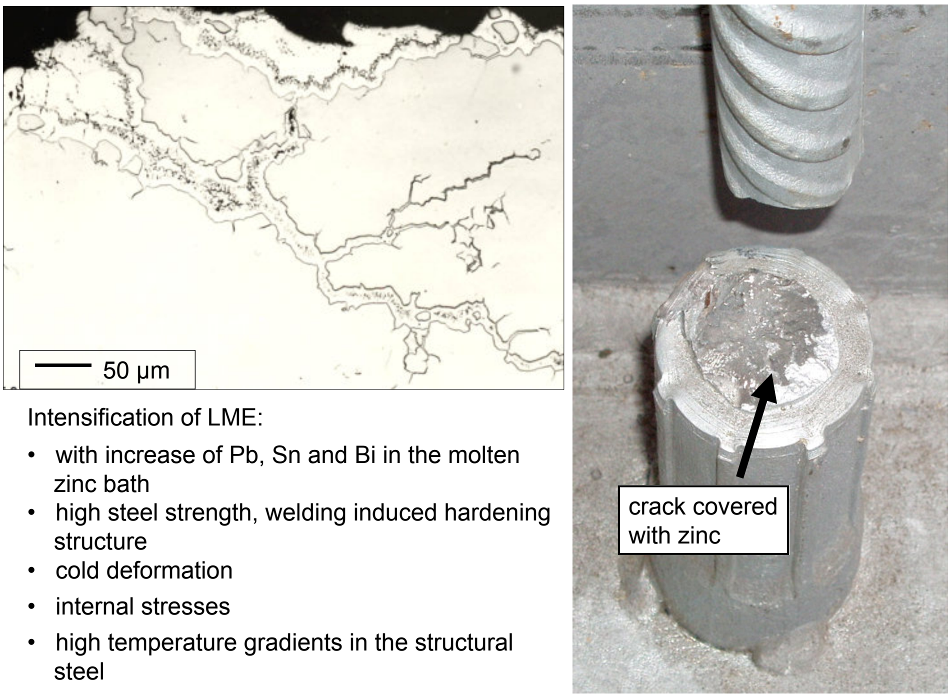
Some standards state that cracking and flaking of the coating shall not be a cause for rejection and that they can be repaired with a zinc-rich primer paint. It is obvious that it is better to galvanize reinforcing bars after bending or as a pre-fabricated reinforcement cage.

To achieve good protection in concrete, the coating should be as thick as possible, but thick zinc layers reduce bonding with the steel base when subjected to mechanical stresses (see above). An external pure zinc layer of at least 10 µm is recommended and a total galvanized layer of at least 80 to 100 µm is necessary to provide suitable protection of reinforcement embedded in concrete. A limit of 200 µm is often recommended as maximum.

There is also the possibility of the zinc bath causing liquid metal embrittlement (LME) of cold deformed reinforcing steels [10]. In the example of LME in Fig. 3.5, the cold deformation results from a clamp joint. Liquid metal induced embrittlement is a liquid zinc assisted intercristalline cracking of the steel, similar to anodic stress corrosion cracking. It mainly occurs in an alloyed zinc bath during the galvanizing process. Especially the elements tin, lead and bismuth are added to the molten zinc bath in order to improve the brightness and uniformity of the coating. These elements also hinder the uncontrolled coating growth that is combined with bad adhesion and result in an uneconomical situation. However, the element tin, lead and bismuth favour the cracking of the strongly cold deformed steel. Further parameters which promote cracking are mentioned in Fig. 3.5.

3.2.2 Mechanical properties

The question may be asked: does the process of hot dip galvanizing influence the properties of the steel itself? As steels are of different grades, different metallurgical composition and sometimes are cold worked, the possibility of changes cannot be excluded. Due to the usual bath temperatures between 450 and 470 °C, and the immersion time of several minutes, ageing and tempering is possible. Ageing may result in an increase of strength and a decrease in ductility, while tempering could give the opposite results.



Intensification of LME:

- with increase of Pb, Sn and Bi in the molten zinc bath
- high steel strength, welding induced hardening structure
- cold deformation
- internal stresses
- high temperature gradients in the structural steel

Fig. 3.5: Clamp joint between steel plate and galvanized reinforcement; steel fracture because of liquid metal induced embrittlement (LME) of galvanized steel. Cracks: zinc enriched with tin (Sn) and lead (Pb)

Nevertheless, the changes are regarded as of nearly no practical consequences. Galvanization of hot-rolled bars, cold deformed wires and welded fabrics do not markedly the performance characteristics (mechanical properties, fatigue behaviour) crucially [9,11-13].

Also, the mechanical properties of Tempcore steel bars, which have an external layer with a microstructure of tempered martensite, galvanized for 10 minutes at about 450 °C, do not change the mechanical characteristics, the values of which are maintained above those required by the standard [14].

Welded fabrics were tested in Germany [11]. Strength values of galvanized fabrics were found to be practically the same as of non-galvanized and tempered fabrics, while the elongation values were slightly better for the galvanized. The strength of the welded joints was not affected. Only cold-worked steel with a tendency to ageing might be embrittled after a certain time. Hot dip galvanizing of such steels will accelerate the embrittlement, and they should be normalised or tempered before galvanizing. Such steels are no longer in common use.

Hydrogen embrittlement is not a problem with normal low alloyed reinforcing steels. The hydrogen introduced in the pickling process is expelled when the steel is immersed in the hot zinc bath. Some quenched and tempered prestressing steels, however, might be embrittled by inclusion of hydrogen. Tests should be carried out before such steels are hot dip galvanized. Generally is recommended not to galvanize reinforcing steels with tensile strength above 800 N/mm^2.

3.2.3 Extreme temperatures

The zinc coating can be continuously exposed to temperatures up to 200 °C without any harm. At temperatures higher than about 250 °C, the zinc crystals anneal through, and there will be no more pure zinc layer. This galvannealing takes place in some minutes.

At higher temperatures a diffusion process takes place in the coating so that the external zinc layer departs from the iron-zinc layers. The iron-zinc layers, when embedded in concrete, are much less stable due to a microgalvanic effect. These layers may disintegrate and are less resistant to chloride attack.

3.2.4 Fatigue

German experience [8,11] indicates that the fatigue performance depends on the type of reinforcing steel. The metallurgical composition of the steel might influence the composition of the zinc-iron layers. When subjected to pulsating stresses, these layers crack. Such cracks act as crack initiators at the steel surface. Another possibility is that the temperature of the zinc bath acts to temper the steel, which may change (improve) the steel's performance.

Ribbed hot rolled bars were tested in Germany in the form of straight bars not embedded in concrete. Galvanized bars showed a decrease in fatigue strength of about 15 % compared to non-galvanized bars. For embedded bent bars (D = 15 d), the result was nearly the same. The reductions are most likely due to surface effects. By the pickling process the original roughness of about 25 mm of the hot rolled surface is nearly doubled. Tests on welded fabrics also showed that the fatigue performance was better when galvanized. The reason could be the positive effect of the zinc bath in reducing welding stresses.

Tests from Finland [15] showed that the fatigue strength of certain structural steels may be reduced by as much as 25 % as a result of hot-dip galvanizing, and that this reduction is independent of the silicon content of steel or the thickness of the zinc layer. As long as the zinc coating is not removed by corrosion, galvanized bars have better fatigue properties in concrete than non-galvanized steels if reinforced concrete beams are tested in seawater [3,15].

3.2.5 Weldability

Though welding can be accomplished by welding through the galvanized coating, the preferred method is to remove the zinc coating in the region of the weld, generally by grinding or grit blasting. However, for welding of galvanized reinforcement all the methods employed for non-galvanized reinforcements can be used. The zinc coating influences the welding; this could require some alterations of the welding parameters. The welding should proceed at a slower rate than normal, as pores may develop due to evaporated zinc and gasses which do not get time to escape before the welded metal solidifies. This problem may be avoided by having a gap of 1.5 mm between the parts to be jointed when CO_2-welding, or of 2.5 mm when using covered electrodes. As zinc easily alloys with copper, copper electrodes have to be frequently cleaned .

Loss of the zinc coating locally in the area of the weld should not significantly affect the protection, provided the exposed area is small compared to the surface area of galvanized steel adjacent to the weld. In areas where the coating has been removed to facilitate welding, and if the loss of zinc coating after welding galvanized steels is large, additional protection by zinc-rich paint or other repair methods [6] could be necessary after cleaning the surface in the "burned" area. It is recommended, if possible, to galvanize reinforcing steel after welding.

3.2.6 The phenomenon of hydrogen evolution [16-18]

Several reports have studied the bond behaviour of hot dip galvanized steel in concrete, for both plain and ribbed bars. The results are rather contradictory. This is due to use of different types of tests (pull-out or beam tests), different type of cements and different ages of the test specimens.

When considering the bond between galvanized steel and concrete, the zinc reaction in the fresh concrete should be considered. Zinc is an amphotere metal and therefore susceptible to alkalies. In aqueous alkaline solutions the corrosion increases with rising pH value (Fig. 3.6). Zinc, however, forms protective coatings made of solid corrosion products in many normal media such as cement mortar by reaction with its environment.

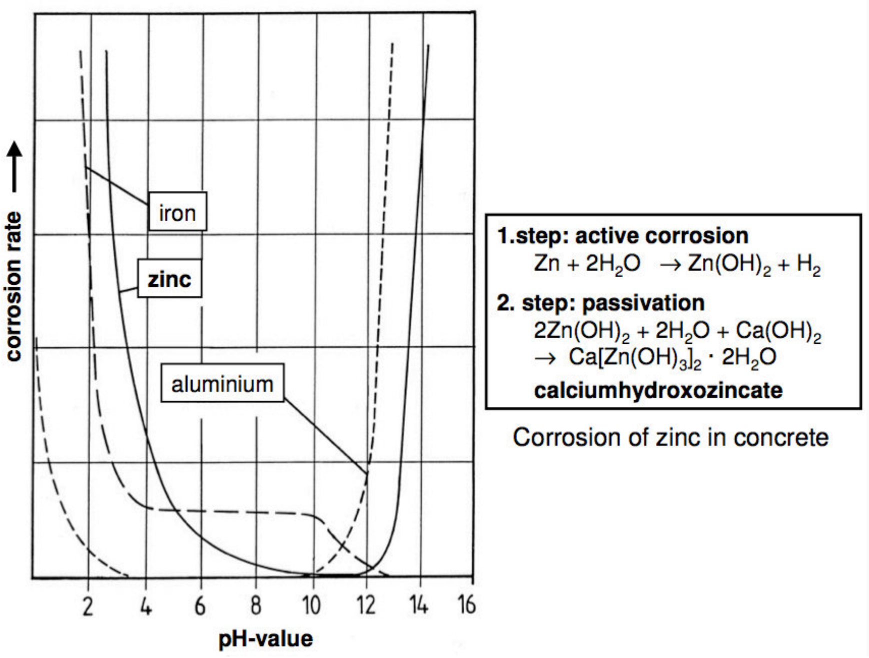


Fig. 3.6: Corrosion rate of metals in aqueous solutions as function of the pH value and corrosion of steel in fresh concrete

Initially, the galvanised coating in fresh concrete will be attacked and dissolved by the alkaline pore water. In this active corrosion phase, zinc-hydroxide („white rust“) is formed and hydrogen is released. As this reaction proceeds, the hydrogen accumulates into small bubbles, which slowly move upwards to the concrete surface provided that the concrete has not been hardened. This may, if the concrete cover is low, result in variations in the texture of the concrete at the surface which may be aesthetically undesirable. The source of hydrogen is the cathodic reaction including water decomposition:

$$Zn + 2H_2O \rightarrow Zn(OH)_2 + H_2$$

$Zn(OH)_2$ has no adequate corrosion-protective capacity.

Subsequently, zinc-hydroxide is converted into calciumhydroxozincate [17,19,20]. These corrosion products passivate the zinc-metal and arrest zinc removal and hydrogen evolution. The intensity and duration of active corrosion in the early stage depends on the alkalinity in a range of pH 12 to 14 of the pore water. As seen in Fig. 3.7 the current density of zinc corrosion in electrochemical measurements, that is the rate of active corrosion of zinc in aqueous solutions or in fresh concrete, considerably increases with increasing pH value of the alkaline solution (the alkaline pore water). The time to reach the passive condition during the setting period also depends on the alkalinity of the cement. In concrete made with alkali-enriched cement, the passivation process may persist for hours or even days longer than in concrete made of low alkali cement. One particular feature of these alkaline solutions, which is relevant for the behaviour of zinc, is that the concentration of Ca^{2+} decreases when the pH value increases. The importance of this is that the presence of Ca^{2+} is needed for the passivation of zinc in alkaline solutions [17].

The conversion of zinc hydroxide in an alkaline pore solution of fresh concrete into calcium hydroxyzincate is as follows:

$$2Zn(OH)_2 + Ca(OH)_2 + 2H_2O \rightarrow Ca[Zn(OH)_3]_2 \cdot 2H_2O$$

It is important that the evolution of hydrogen at the interface between the galvanized bar and the concrete, simultaneous with the process of passivation by a film of calcium hydroxozincate, may slightly reduce the adhesive bond at an early age [20,21].The formation of calcium hydroxyzincate and the hydrogen, that is released at the interface between the bars and the concrete, may delay the setting and reduce the early strength of the concrete close to the bar. The consequence is a slight reduction of the adhesive bond at an early age. The hydrogen, however, loosens the surrounding structure of the concrete, resulting in reduction of friction for early bond action and shearing strength between the galvanized bar and concrete. Through further reactions the zincate is evidently included in the hydration products by physical and chemical reactions, which leads to a higher strength of the concrete close to the coating surface [12,22] and finally to a better bond between zinc and concrete than with non-galvanized bars [21,23]. In this process, chromate is to be regarded as a reaction-inhibiting compound, and therefore the chromate content of the cement is important [18].

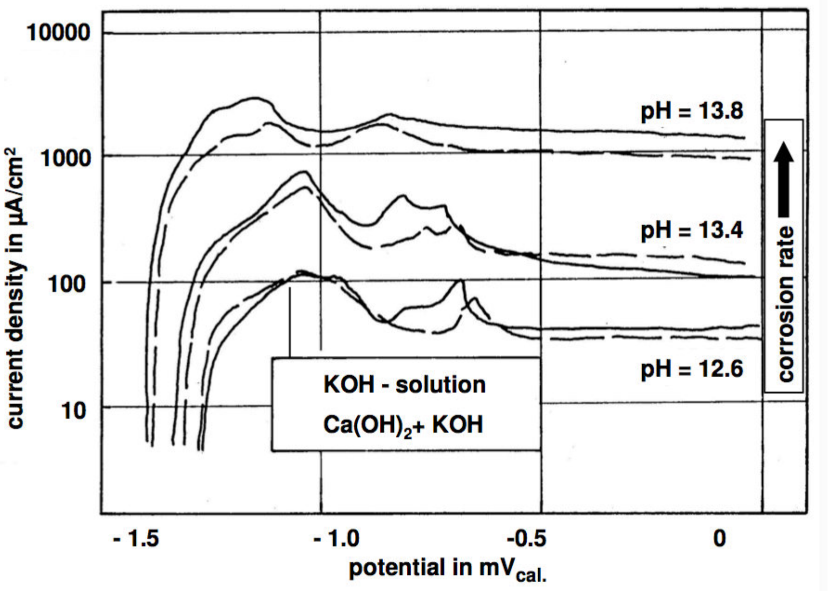


Fig. 3.7: Zinc corrosion in high alkaline aqueous solutions [24]

Passivating agents such as soluble chromates can inhibit the reaction of zinc with the alkali concrete [1,16,20,25]. In former times, soluble chromates were present in most cements to a greater or lesser extent. In these cements, with soluble chromates between about 2 and 25 ppm (values for German cements), strong zinc corrosion and hydrogen evolution in fresh concrete was suppressed, the suppression increasing with increased solution of chromates. It is assumed that a combination of alkalinity and chromate content of the cement is the determining factor. The higher the alkali content and the lower the soluble chromate content, the stronger and the longer the hydrogen reaction and the later the passivation is finished.

However, it was pointed out that chromates, which are the most effective passivating agents for zinc, are hazardous to human health and may cause a contact allergy, chromium eczema [26]. Therefore the European Community limited the contents of water-soluble hexavalent chromium in cements to very low levels lower than 2 ppm. For this purpose an excess of iron (II) sulphate is added. Nowadays in Europe, chrome free and chrome reduced cements are used for reinforced concrete.

Studying newer publications [18] it can be concluded, that in concrete where chromate reduced cements had been used the galvanized coating will become passive and hydrogen evolution stops within a few hours to several days [5,27-29]. Fig. 3.8 demonstrates the time of hydrogen evolution of galvanized steel embedded in concrete made of chromate-reduced cement. After 1 to 2 days, the hydrogen evolution finished and the galvanized bars were passivated, independent of the type of coating. The two types of coatings (Fe-Zn alloy layers with and without the outer pure zinc layer) were investigated because the pure zinc provides the most effective passivation in contact with alkaline solution, while the underlying Fe-Zn layers are less stable particularly in the presence of chlorides which selectively attack them.

Since the introduction of the chromate reduced cements, some irregularities occur which are connected with this action:

- alterations in the concrete surface as a consequence of hydrogen bubbles which in the unsolidified concrete come up from the reinforcement,
- and an effect on the bond behaviour.

In particular, concerns are often expressed that hydrogen evolution will reduce the bond strength of galvanized steel in concrete. However, extensive research on this field has demonstrated that there is no reduction in bond strength of galvanized bars in comparison to non-galvanized steel (chapter 3.2.7). The reaction of zinc with the alkaline concrete and hydrogen evolution at the metal-to-concrete interface can be inhibited at an early stage, resulting in better bond, by passivating agents such as soluble chromates [20,21]. In past times it has been suggested that the problem of hydrogen evolution can be overcome by adding chromate to the concrete mix or by giving the bars a chromate passivation treatment by quenching the freshly galvanized bars into a solution containing 0.2 % sodium dichromate in water or in a minimum of 0.2 % chromic acid solution [1,16]. With regard to these two methods to passivate galvanized bars, the second is more suitable and it is also required by existing standards. Particularly for health and environmental reasons, the addition of chromates to the concrete mix must be considered unacceptable.

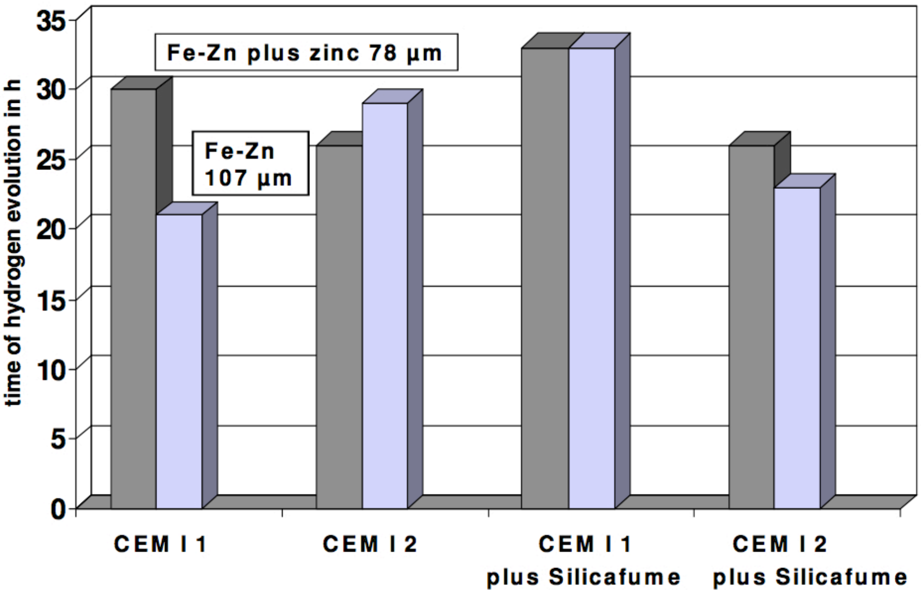


Fig. 3.8: Time of hydrogen evolution of galvanized steel embedded in concrete made of chromate reduced cement [28]

Chromate treatment of galvanized steel is a requirement of ASTM A767 and ISO 14657 (chapter 3.2). However the practice of chromating the reinforcement, whether by applying it directly on the steel surface or to the concrete mixing water, is not at all necessary, because galvanizing has no adverse effect on bond strength.

3.2.7 Bond behaviour [16,18]

The bond between the reinforcement and the concrete is one of the most essential properties contributing to the successful functioning of the reinforced concrete system. If the bars are smooth, the main contributions to bond strength come from the chemical adhesion and the friction resistance occurring between the bar surface and the concrete. If the bars are ribbed, the bearing capacity of the concrete between the ribs and the shear strength of the concrete cylindrical surface located between the ribs are responsible for bond. In the use of galvanized reinforcement, the principle issues relating to bond behaviour concern whether there is any significant influence of galvanizing on the development of bond and slip respectively: the time to develop full bond strength and the ultimate bond capacity.

In many pull-out tests, the bond behaviour of non-galvanized and galvanized steel was measured and compared. In some earlier publications on smooth wires, e.g. [21,30], it was reported that when applying cements with low chromate content the evolution of hydrogen gas reduces the bond strength of galvanized wires in concrete. It was noted [30,31] that hydrogen evolution from the coating and bond behaviour can be effectively improved by treatment of the freshly galvanized steel with chemicals, the most common of which are chromate salts.

Extensive research in the last twenty years has universally demonstrated that there was no reduction in bond strength for galvanized bars compared to equivalent non-galvanized bars. Mostly galvanized smooth bars had superior bond strength in comparison to non-galvanized bars [5,13,16,22,23,32-37]. An important aspect of this research was that the hydrogen evolution from galvanized steel immersed in concrete made of Portland cement can, if at all, delay the development of strength and adhesion bond for only few hours. In Fig. 3.9, typical results for slip characteristics and bond of ribbed galvanized and non-galvanized steel are demonstrated. Two types of cement with different chromate contents were chosen. The adhesion bond slips until about 0.01 mm and the shearing bond with slips between about 0.1 and 1 mm are to be distinguished. The adhesion bond depends on chemical and physical reactions between zinc and components of the cement. The shearing bond is controlled by the shape of the ribs. These pull-out tests in early age concrete after 7 days show:

- in comparison to non-galvanized steel the shearing bond of the galvanized steel is the more greater the higher the chromate content of the cement,
- because of thicker coatings of pure zinc at the base of the ribs the shearing bond may decreases a little.

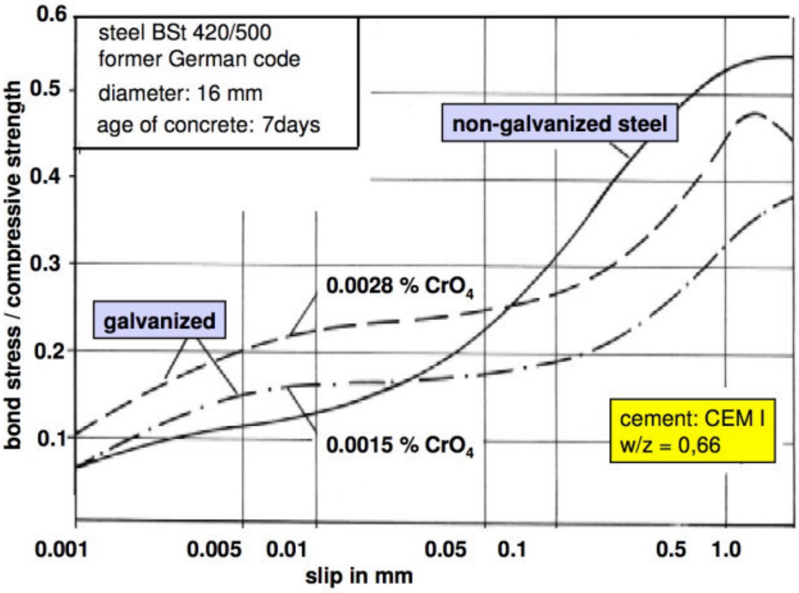


Fig. 3.9: Bond of non-galvanized and galvanized ribbed reinforcing steel after 7 days [13]

No pull-out tests from concrete made of chromate reduced cements with lower than 2 ppm chromate have been carried to date. But extensive tests exist on plain and ribbed non-galvanized and galvanized bars [33] where a type of cement with a relatively low chromate content of 3 ppm was used. In addition selected admixtures for concrete were added to the concrete mix in the highest permissible dosage. The tests were performed 1, 2 and 9 weeks after the specimens had been concreted, so that the effect of time on the reaction between zinc and calcium hydroxide could be detected.

It can be seen in Fig. 3.10 that, even after only 7 days, the bond stresses of the smooth galvanized bars were always above the corresponding values for the non-galvanized bars. In the case of ribbed bars, the bond stresses of non-galvanized and galvanized bars after 7 days were of the some order. Later on, the bond stresses of the zinc coated bars further increases.

All tests showed the bond behaviour of galvanized bars to be, if anything, better than of non-galvanized ones. There seems to be no negative influence on bond of galvanized reinforcement, if chromate reduced cements are used.

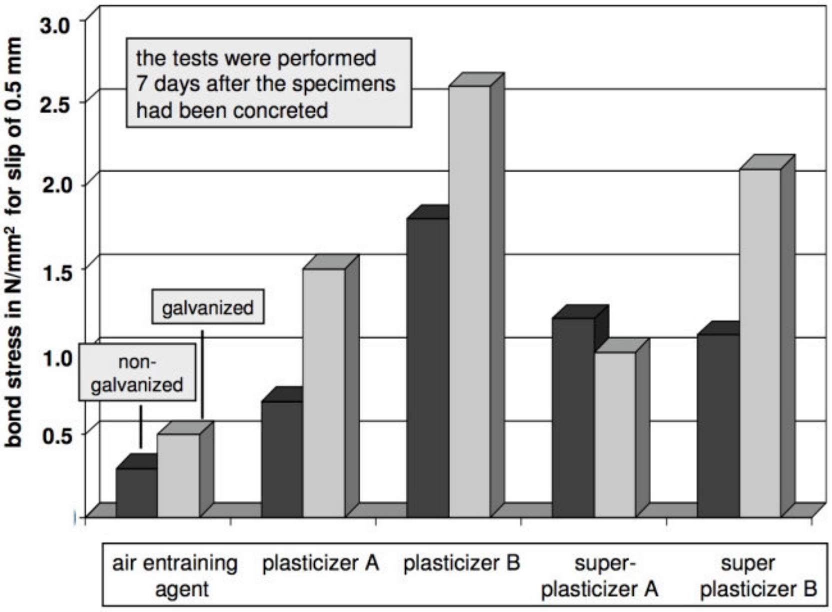


Fig. 3.10: Results of pull-out tests of smooth non-galvanized and galvanized bars, d= 20 mm, specimens concreted with different admixtures, cement with low chromate content of 3 ppm [33]

3.3 Current specifications

Standards for hot dip galvanized reinforcing steel exist in several countries, for example in the Australia/New Zealand (AS/NZS 4680), Canada (CAN/CSA G164), France (NF A35-025), Germany (Zulassungsbescheid N° 215 100-8), India (IS 12594), Italy (UNI 10622), South Africa (SABS/ISO 1461), Sweden (SS-EN ISO 1461), UK (BS ISO 14657) and USA (ASTM A767). In some of these countries, hot dip galvanizing of reinforcement falls under a general galvanizing standard.

The various standards do not differ substantially, from one to the other, and the differences that can be found mostly concern the values of grams per square meter applied and therefore the thickness of the zinc coating and the proof tests for qualifying the final product from the quality standpoint. For structural sections heavier than 5 to 6 mm thick, which would include reinforcement, a minimum average coating thickness in the range 600 to 610 g/m^2 is specified, which equates to a coating thickness of 85 to 87 µm. Similar requirements are in ISO 14657 for bars greater than 6 mm in diameter. In Germany, a minimum average mass of the coating shall be 610 g/m^2 (85µm), and no place shall exceed 200 µm thickness.

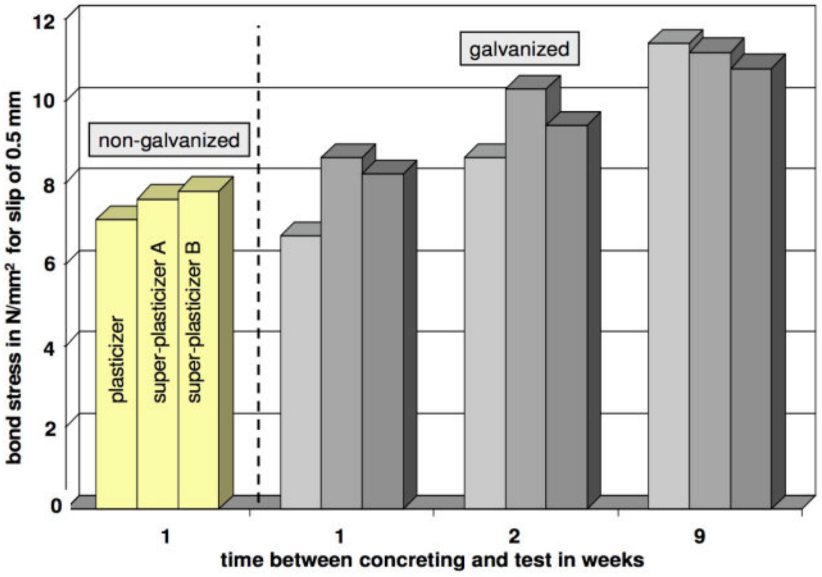


Fig. 3.11: Results of pull-out tests of smooth non-galvanized and galvanized bars, d = 20 mm, specimens concreted with different admixtures, cement with low chromate content of 3 ppm [33]

3.4 Corrosion protection behaviour [1-3,17]

3.4.1 Mode of action [1,3]

A zinc coating retards the onset of rebar corrosion in a corrosive medium, carbonated and/or chloride containing concrete, only if zinc previously creates a stable protective film in the alkaline concrete. Passivation of zinc reduces the zinc corrosion of the normally unstable zinc, but zinc may corrode if the environment is corrosive.

Compared to the corrosion mechanism of non-galvanized steel bars, when the galvanized bars are used embedded in concrete, there is an additional phase between incubation period and propagation, indicated as protection, during which the zinc coating sacrifices itself, thereby protecting the underlying steel until the zinc has been fully dissolved. The beneficial action of galvanizing takes place, however, even during the first phase of incubation during which the zinc's passivity is maintained even at pH values below 11, the range in which steel loses its capacity to passivate.

It is important to note that during the period when the zinc coating corrodes, unlike that which happens in the uncoated steel reinforcement, the zinc corrosion products are less expansive and slightly more soluble in the concrete environment than rust, and may therefore diffuse some distance from the metal-to-concrete interface. In this way the net volume increase and the splitting pressure due to corrosion is reduced [18].

In a chloride containing concrete however, zinc coatings may completely corrode locally. Therefore steel, in theory, may be protected because of the cathodic protection by sacrificial dissolution of zinc. In any case , in chloride containing concrete, no cathodic protection was observed which could protect damaged areas of zinc coating. After local corrosion of zinc, strong pitting corrosion took place [1,38]. However, on comparison within a single reference system, the models of behaviour under corrosion of reinforcing in concrete, it may be stated that the galvanizing of steel bars lengthens the service life of a reinforced concrete structure. This therefore contributes to increasing its durability.

The mode of action is widely accepted by the international literature on the basis of the higher corrosion resistance of galvanized steel over ordinary steel bars when the concrete is carbonated and/or exhibits the entrance of chlorides [39].

3.4.2 Alkaline concrete without chloride [18-20,24,29,40,41]

In fresh concrete, the zinc coating firstly dissolves in the alkaline pore water. This active corrosion results in a uniform loss of zinc of about 5 to 10 μm. Corrosion products formed may seal the surface, thus passivating the metal and arresting the evolution of hydrogen (see chapter 3.2.4). Passivation is due to the formation of a layer of calcium hydroxyzincate on the zinc surface, which inhibits further corrosion. As a consequence, zinc corrosion is reduced to a very low rate.

The time to reach passive conditions with a very low corrosion rate during the setting period depends on the alkalinity of the cement. In fresh concrete the pH value of the pore-water is between 12 and 14. In concrete made with cement enriched in soluble alkali, the film formation is temporarily inhibited during the setting period and the active corrosion of zinc, with the evolution of hydrogen, persists longer. According to pH value of the aqueous pore solution between periods of a few hours to several days, the corrosion rate decreases towards levels measured in concrete manufactured with low alkali content cement [29]. Then, in the hardened concrete, the corrosion rates of galvanized bars embedded in concretes manufactured with different cements tend to equalize, and the values will depend on the concrete parameters and environmental conditions (i.e. water/cement ratio and humidity).

It is also reported [17,41] that when the pH value is 12.6, the surface is totally covered by crystallized corrosion products during the first one or two days. As the pH value increases, the size of these crystals also increases. They then cannot seal the surface so perfectly, leaving small zones of the surface without protection. Just above the threshold value of about 13.3, the corrosion products appear as isolated crystals which cannot seal the surface. Consequently the metal is not sufficiently passivated, and the zinc dissolution continues at a higher rate. The corrosion rates remain high enough to lead to the total dissolution of a galvanized coating in some years [17,41], if the concrete was made with cements giving pH values up to 13.8. As can be seen in Fig. 3.7 and Fig. 3.12 above a threshold value at about pH=13.2 the zinc coating dissolves quickly in an active state, and the coating may disappear totally in a short time.

This relation between alkali content and corrosion rate might help to solve the controversy regarding the stability of galvanized reinforcement. It may explain the fact that as most North American cements have low alkali contents, galvanized reinforcement has been mostly successful there.

It should be said that other researchers do not confirm that high alkalinity increases zinc corrosion in the long run [29,34]. From exposure tests of galvanized reinforcement in concrete produced with cements of an extreme high alkalinity it was concluded that passivation of zinc is delayed all the more the higher the pH value of the aqueous pore solution. However, passivation will take place in any case. From the application of cements with higher alkalinity, it cannot be concluded that the galvanized reinforcement is not durable in the alkaline media.

The hexavalent chromium content in the cement influences the corrosion rate of galvanized steel only in the first days after casting (see chapter 3.6), but seems to be ineffective after the setting period of the concrete.

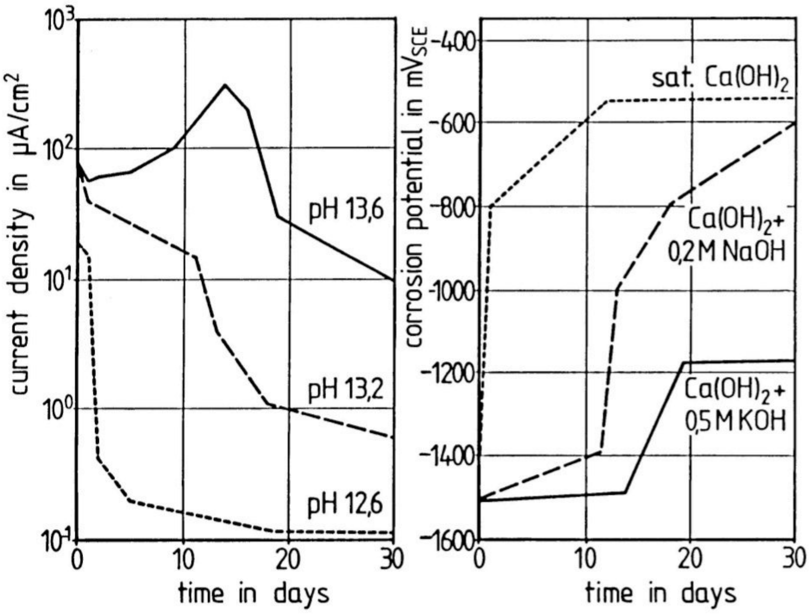


Fig. 3.12: Corrosion current density and -potential of galvanized reinforcing steel in alkaline solutions with pH 12.6, 13.2 and 13.6 [41]

3.4.3 Carbonated concrete [4,24,42]

Carbonation of concrete is caused by the reaction of the atmospheric carbon dioxide with the alkaline substances of the pore water and the phases of the hydrated cement (silicates, aluminates and ferrite-aluminates). This results in a reduction of the pH value of the aqueous solution of the capillary pores. When the pH value drops below the level required for passivation, which typically is about 11.5, and the other parameters necessary for the corrosion process are present (oxygen, water, electric potential), uncoated steel corrodes. The corrosion products lead to the disruption of the concrete cover.

In special laboratory and exposure tests, the behaviour of galvanized and non-galvanized bar reinforcements have been compared in carbonated concrete [24,42-44]. The results in Fig. 3.13 come from British investigations in industrial environments. The carbonation depth in the lightweight concrete after 14 years was 12 - 27 mm. In the carbonated zone (cover 13 mm) the corrosion loss of galvanized steel was significantly less than that of non-galvanized steel, but higher than experienced in the alkaline zone (cover 25 and 38 mm).

In unpublished tests by the author, galvanized bars were embedded in prefabricated reinforced components of lightweight aggregate concrete with an open structure and cover between 15 and 50 mm. The beams were stored in open air. After 10 years, independent of the thickness of concrete cover, the average loss of zinc coating was about 30-40 µm. The rate of zinc corrosion was decreasing. The lifetime of the zinc coating with average coating thickness of 140 µm was estimated to be at least 50 years.

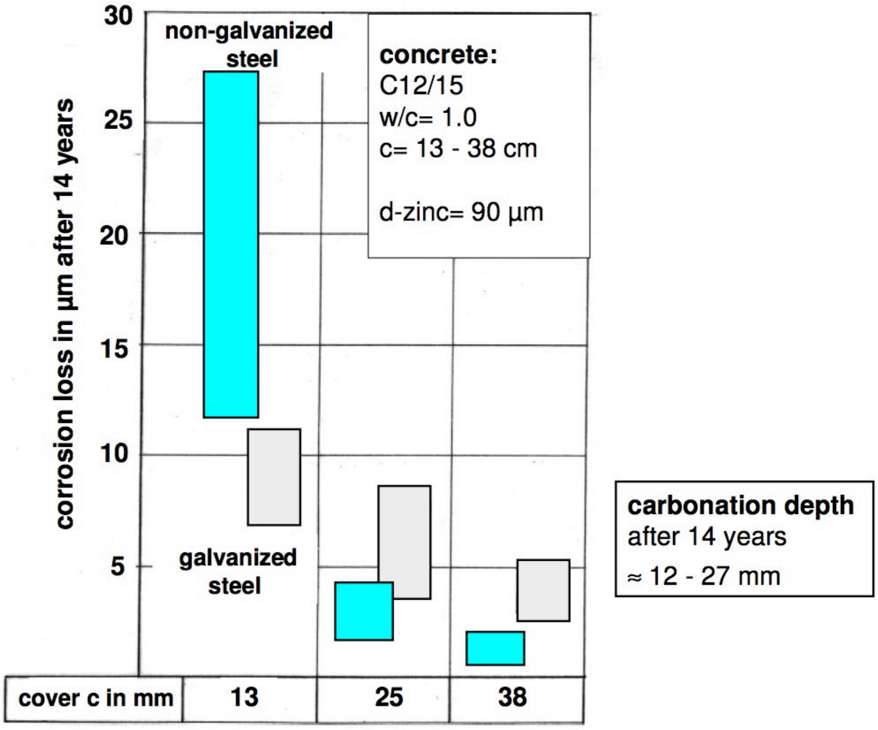


Fig. 3.13: Metal wastage of non-galvanized and galvanized reinforcing steel in lightweight concrete after exposure [44]

Fig. 3.14 summarises the results of this work. In the carbonated concrete, the corrosion rate of galvanized steel is significantly lower than that of non-galvanized steel, but somewhat higher than that of galvanised steel in alkaline concrete. The zinc coating remains passive in completely carbonated concrete. An important characteristic of zinc corrosion in carbonated concrete is the uniform kind of the attack (Fig. 3.15) and also the very low corrosion rate. Theses aspects make galvanized steel reinforcements exceptionally suitable for use in carbonated concrete.

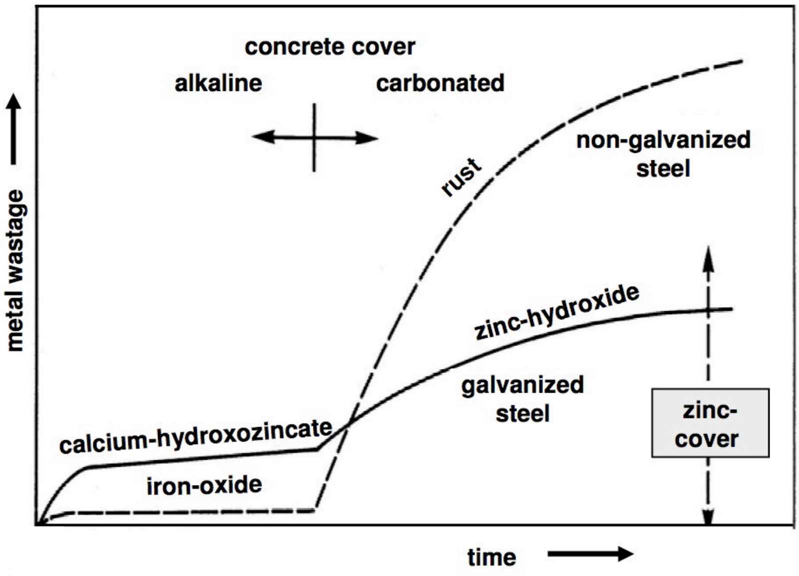


Fig. 3.14: Corrosion performance of non-galvanized and galvanized steel in concrete [3]

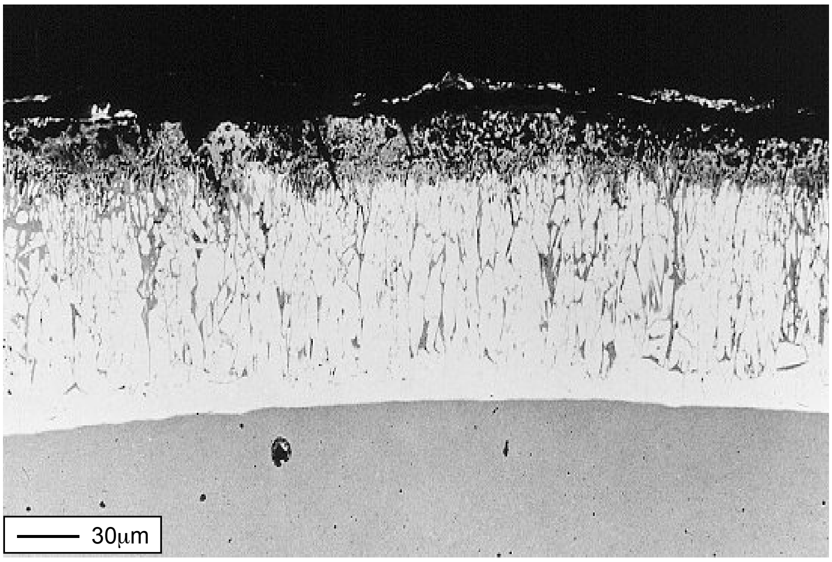


Fig. 3.15: Uniform corrosion of galvanized steel in carbonated concrete [3]

In conclusion, galvanized reinforcement is of advantage compared to non-galvanized bars where a quick carbonation of concrete is to be expected. Usually this is the case if the concrete is not dense, as with lightweight concrete, or if the cover is small. Then the zinc coating delays an early corrosion, and an associated development of concrete cracks and scaling.

3.4.4 Chloride-containing concrete [1,17,42,44-48]

Chlorides are the most aggressive ions in reinforced concrete, and the most frequent cause of reinforcement distress. Marine environments, or the use of de-icing salts, are the most common sources of intrusion of chloride from the outside. The presence of chloride ions (Cl^-) is well recognised as causing accelerated attack on reinforcing steel. Even at high pH values, the chlorides depassivate the steel. They also increase the conductivity of the concrete electrolyte, thereby speeding up the rate of attack.

The threshold value of the chloride ions, which initiates corrosion, depends on a variety of parameters, e.g. the pH value of the pore solution, oxygen access and others. The often-reported chloride threshold for mild steel, which leads to non-acceptable corrosion attack, is between 0.5 to 1.0 mass-% of the cement content. In most specifications, a lower value is recommended as a threshold value.

Corrosion of galvanized steel in chloride-containing concrete is less rapid and less extensive for a substantial period of time than that of non-galvanized steel. The use of galvanized bars therefore guarantees a significant reduction in the rate of cracking and spalling of reinforced concrete containing chloride. Consequently deterioration of concrete is less likely to occur.

Zinc, however, can be depassivated and attacked in the presence of chloride ions. It should be distinguished between chlorides added in the mix, and chlorides which later penetrate from the outside. Those added in the mix are present during the formation of zinc corrosion products, and may therefore attack the coating before and during the formation of the protective layer. Those penetrating from the outside find this layer already formed and therefore may be less aggressive.

The most important characteristics of chloride corrosion of galvanized steel are the aspects of corrosion in form of the pits (Fig. 3.16) and a preferential disaggregation of the alloyed layers at some particular spots (Fig. 3.17). The reason for this might be that the alloyed layers are less resistant against Cl-attack than the pure zinc layer [17]. Galvannealed coatings without an outer layer of pure zinc are destroyed very quickly when they are used in chloride-containing concrete.

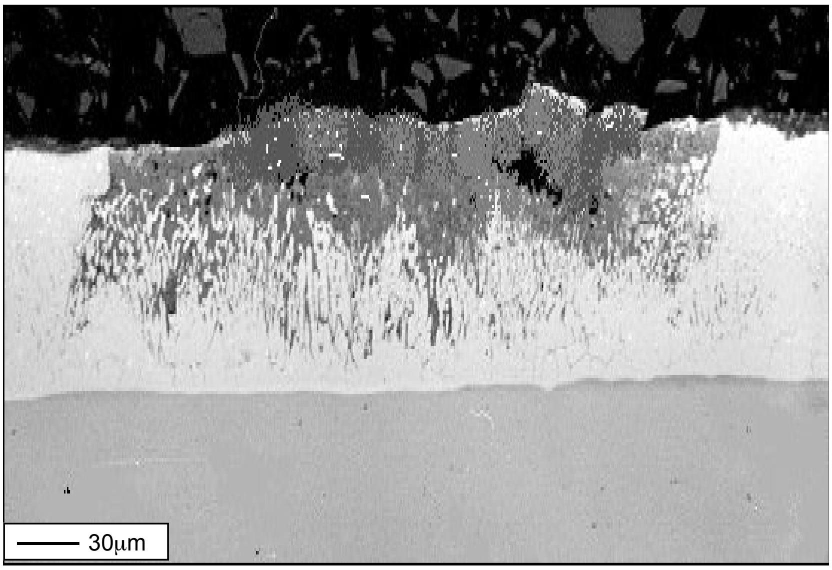


Fig.3.16: Pitting corrosion of galvanized steel in chloride containing concrete [3]

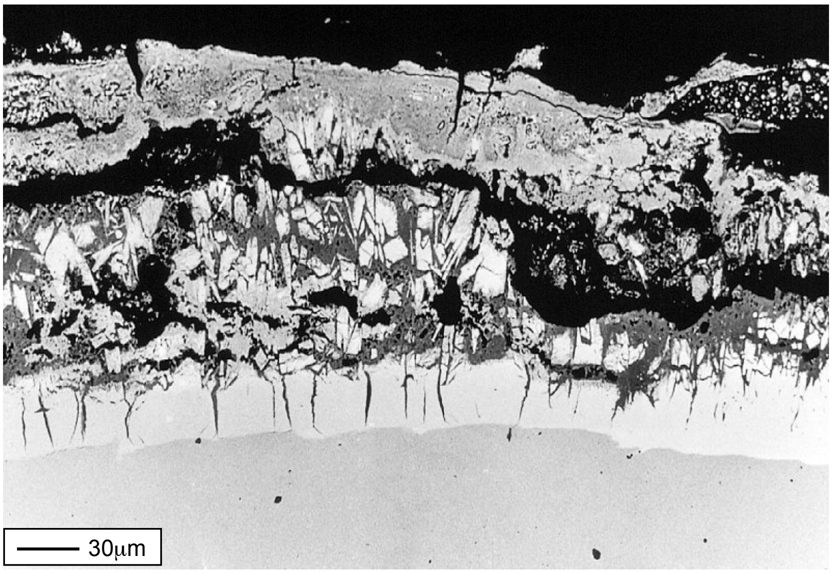


Fig. 3.17: Zinc-corrosion in heavily chloride-contaminated concrete [3]

Therefore, beside the type of cement (see below), the rate of zinc-corrosion depends on further factors such as the quality and thickness of the pure zinc layer. The most durable zinc coatings are those with a thick external layer of pure zinc. Galvannealed coatings may be quickly destroyed because the iron-zinc layers are less resistant to chlorides when embedded in concrete [1]. Therefore, once again, the most resistant part of the zinc coating is the layer of pure zinc, while the alloyed layers form the weakest part.

With respect to the type of cement, the higher the alkali content, the lower the susceptibility to chloride attack should be expected. If there is a high pH value, most likely a lower chloride content is sufficient to initiate the corrosion. However, calcium aluminates (AC_3) and ferrite-aluminates (AFC_4) react with chlorides. Hence the corrosion rate will depend on the total amount of AC_3 and AFC_4, as well as the alkali content of the cement. To ensure the corrosion resistance of galvanized steel in concrete, the reactivity of the zinc coating should be lowered by selecting the correct cement type (alkali content not too high), or by the passivation treatment of hot dip galvanized steel. On the other hand, it should be noted that, now, due to environmental regulations, the alkali content of cements has increased as compared to the 1980s. It is therefore difficult to find cements with a low alkali content on the market. A good method to make the alkalinity of the concrete compatible with the employment of galvanized reinforcements is by adding silica fume to the mix. This substance not only lowers the alkalinity of the mix, but also improves the quality of the concrete.

Marine exposure tests of concrete beams reinforced with non-galvanized and galvanized steel [44,45,47] have shown the threshold chloride concentration for depassivation of zinc to be greater than the level required for attack of uncoated steel. If the limit of the chloride content under these conditions is set at 0.5 to 1.0 % (by weight of cement) for uncoated steel, it would seem reasonable to set a limit of about 1.5 % for galvanized steel (Fig. 3.18 and 3.19). Consequently, galvanized steel in concrete tolerates higher chloride concentrations than uncoated steel before corrosion starts. However, the results indicated that galvanized steels are unsuitable for use as corrosion resistant reinforcements in concrete heavily contaminated with chlorides. If the chloride content exceeds about 1.5 % in weight of cement, the corrosion rate increase rapidly.

Some long-time exposure tests have been performed. Concrete specimens with non-galvanized or galvanized bars with cover 30 - 90 mm were exposed for 12 years from 0 to 14 m above the lowest sea water level [49]. In areas more constantly wetted by seawater, the corrosion was small. Above the highest water level, where the cover intermittently could dry out, the corrosion was pronounced. Here the intensity of corrosion of the galvanized bars were roughly 75 % less than of the non-galvanized bars.

To investigate the effects of the use of de-icing salt on bridge decks, horizontally placed slabs with non-galvanized or galvanized bars were subjected for many years to spraying 15 times each winter with water including 0.5 kg/m^2 of $CaCl_2$ [50]. With a cover of 1.3 cm, corrosion occurred after 2 years on the non-galvanized bars, with scaling after 3 years. After 6 years the non-galvanized bars showed serious local corrosion with a pitting depth of 1.6 mm on the upper part of the bars where the chloride content was 0.4 %. The galvanized bars had lost only 5 µm of their coating after 6 years. With a cover of 3.8 cm, about 0.1 % chloride was measured after 6 years, and neither non-galvanized nor galvanized bars were attacked to any practical degree.

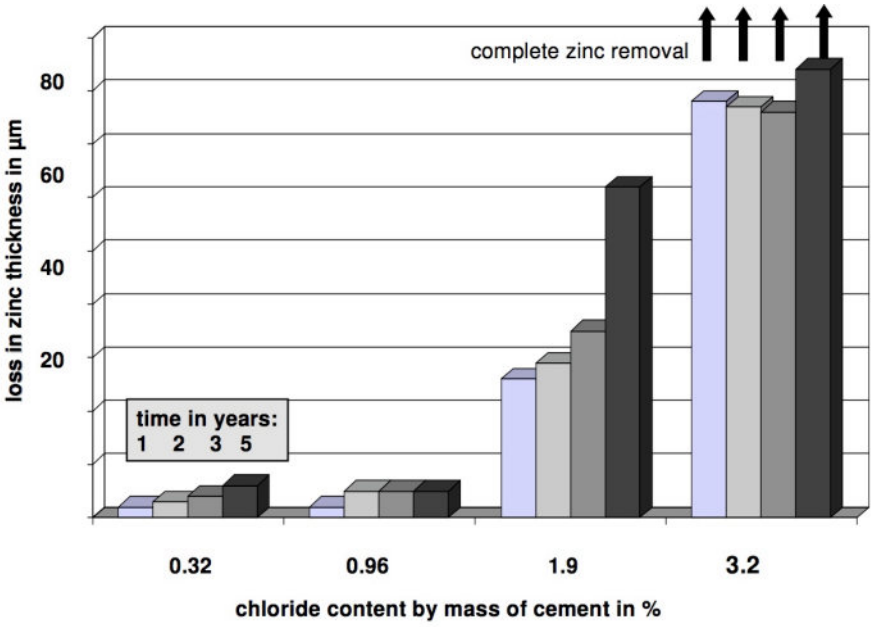


Fig. 3.18: Influence of the chloride content on the corrosion of galvanized reinforcing steel stored in concrete in the open air [44]

In [44] the influence of chloride content on the corrosion of non-galvanized and galvanized reinforcing steel embedded in normal-weight concrete specimens (concrete cover 10 and 20 mm) stored in the open air was investigated (Fig. 3.18). From 1 to 3 chloride content (in % of cement content) concrete cover badly corroded non-galvanized steel showed cracking and spalling after 5 years. The specimens reinforced with galvanized reinforcement showed no visible damage to the concrete. Serious zinc corrosion was noted above 1- 2 % chloride.

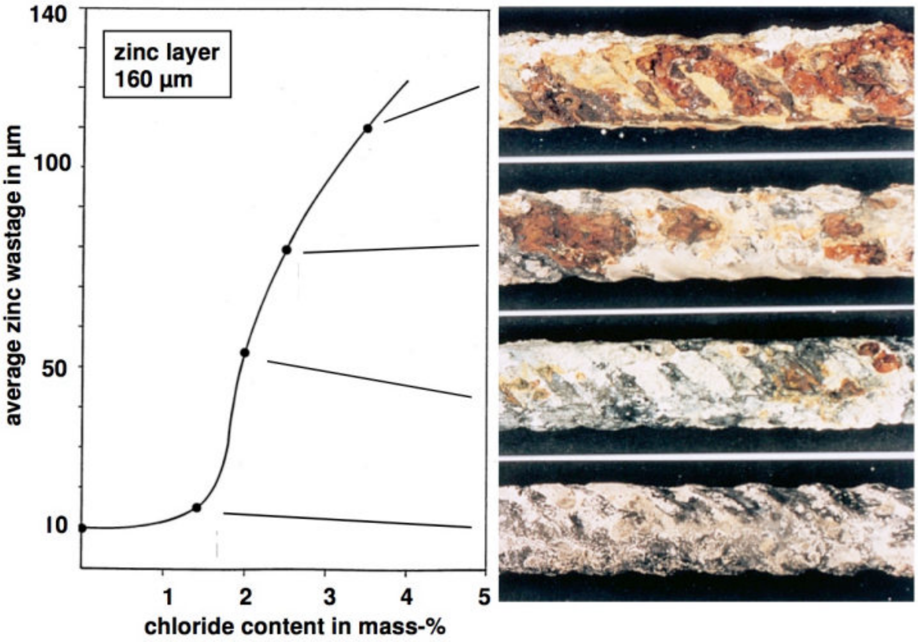


Fig. 3.19: Zinc wastage of galvanized reinforcing steels after 2.5 years embedded normal-weight concrete as a function of chloride content after seawater exposure (concrete cover 15 and 25 mm) [47]

In a survey of a number of old marine structures, galvanized bars had been exposed to chloride contents as high as 2.2 % by weight of cement over a period of 10 to 20 years with a loss of coating thickness far less than 10 %, and with no record of failure [2]. This should be compared to those lower chloride levels of 0.5 - 1.0 %, which leads to severe corrosion of non-galvanized steel in similar circumstances.

A general conclusion might be that even in concrete rather highly contaminated with chloride, galvanized steel usually performs well. Should it fail, galvanization has always delayed the onset of the state of active corrosion compared with non-galvanized bars. The protection rendered by the galvanization is limited in time.

3.4.5 Cracks in concrete

In principle, cracks contribute to the corrosion process. The sides of cracks will quickly carbonate, and represent spearheads of the carbonation front. Moreover, in chloride-contaminated environments, they represent a quick way for the chlorides to reach the reinforcement. The result may be localised corrosion damage within the crack. In the presence of chlorides, a crack in the concrete cover always represents a special corrosion risk for a galvanized reinforcement [45,47].

The width of the crack is of minor importance. Whether a particular crack will lead to a localised damage or not will depend on other parameters such as concrete quality or cover thickness. Fig. 3.20 shows that the corrosion of galvanized bars increases at about 0.2 mm crack width at a cover of 2.5 cm, and at 0.3 mm width at 5.0 cm cover.

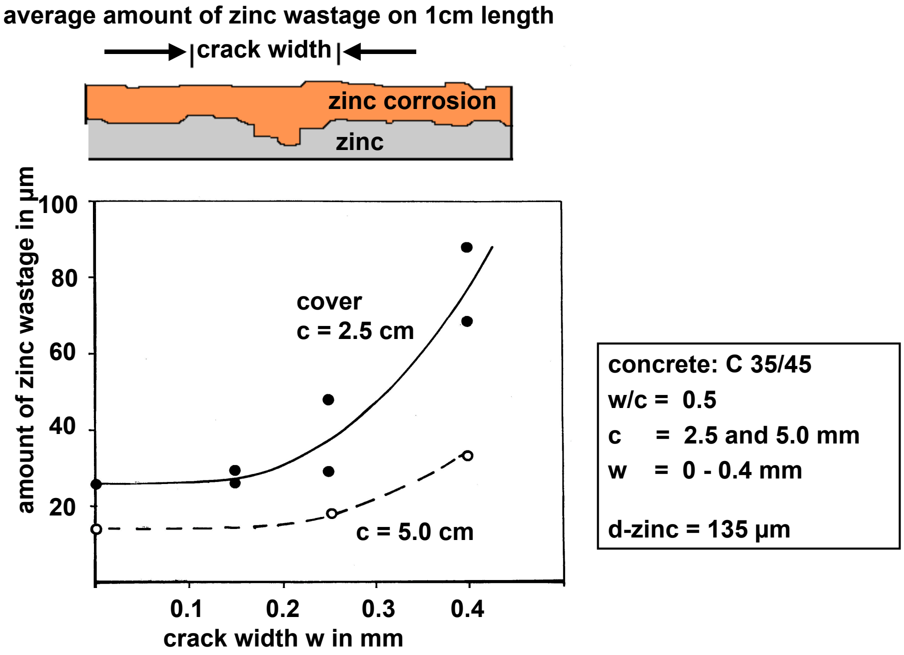


Fig. 3.20: Corrosion of galvanized reinforcing steels in cracks of concrete under condition of seawater splash zone [47]

3.4.6 Cracks in the zinc coating

With respect to the effects from cracks, holes or scaling of the zinc coating on the durability, the current knowledge does not seem to be sufficient to give a trustworthy answer. At any rate in chloride containing concrete, no cathodic protection was observed which could protect damaged areas of zinc coating. After local corrosion of zinc, strong pitting corrosion took place [38].

3.4.7 Resistance to galvanic corrosion

Sometimes, the use of galvanized steel bars is proposed as an external skin reinforcement electrically connected with the non-galvanized steel reinforcement positioned more deeply in the concrete. Because of macro coupling, the non-galvanized steel which is in a passive state and has a higher corrosion potential in contact with the galvanized steel tends to temporarily accelerate the corrosion rate of zinc during the setting period when it is in an active state and the corrosion potential of zinc is low. After the protective layer is formed on the zinc surface and its potential rises, the potential difference between both metals will be slowed down. The risk of detrimental effects due to galvanic macro coupling in chloride free concrete after that is strongly reduced [3].

3.5 Practical experiences with application

Hot-dipped zinc (galvanized) coatings for reinforcing bars have been used over the last fifty years in all countries which consume significant quantities of reinforcement. It seems to be mostly applied in the USA, Australia, Bermuda, Netherlands, Italy, UK and Germany. In the USA, about 2 % of ordinary reinforcement is galvanized. For Europe, the estimate is 1 %. At present the consumption of galvanized reinforcing steel is stagnant. The main applications are for concrete bridge and highway constructions exposed to high levels of accumulated chlorides due to the application of de-icing salts or in marine exposure. It is also used for industrial constructions such as cooling towers, chimneys, paper mills and chemical processing plants and a host of buildings of all types.

Contradictory evidence of the performance of galvanized steel in concrete has been reported in the literature. Whilst laboratory and field studies have suggested that galvanizing can only delay the onset of the start of active corrosion compared with non-galvanized steel, and that its performance would not be cost effective, galvanized steel has often been used successfully in practice [1,2,51-53]. But there are other structures where galvanized reinforcements have not performed well, and have required costly maintenance programmes.

Galvanizing of reinforcement was introduced to improve the service life of concrete structures in tropical and marine environments in America. The first practical use of galvanized reinforcement was reported in 1931 and concerned a dock in Bermuda [2]. The hot and wet marine climate of those islands, combined the use of 'coral' aggregates, reduced the durability of concrete structures. As the first experience was successful, the use of galvanized reinforcement was recommended by the Department of Public Works of Bermuda, and consequently widely used. When their airport was partly demolished after 15 years of service, the galvanized bars revealed good performance. Further data from Bermuda has verified the long-term durability of galvanized reinforced concrete in marine environment. Commencing shortly after World War 2, a number of docks, jetties and other infrastructures were constructed using a mix of galvanized and non-galvanized bars. A survey undertaken in 1991 showed that the galvanizing was providing continuing corrosion protection to reinforcement at chloride levels well in excess of threshold levels for non-galvanized steel [53].

Due to these encouraging experiences, use of galvanized reinforcement in bridge decks was extended to the USA and Canada. In their cold areas large amounts of de-icing salts are used to improve the safety of roads and motorways. This leads to early corrosion of reinforcement in bridges and reinforced concrete pavements. Even when using a thick, dense concrete cover of low permeability, the bars started to corrode within the first 10 years. Such deterioration necessitates premature and very costly repair and even rebuilding of these structures at a cost of billions of dollars.

Numerous bridges are built in the USA and Canada with galvanized reinforcement. Many of them, e.g. bridge decks, were inspected some years after erection to check their performance. Generally, it is reported that where non-galvanized steel was used, there was evidence of corrosion even in the presence of low amounts of chloride. However, when galvanized steel was used, no evidence of significant corrosion or concrete distress was found.

The Portland Cement Association commenced a study in 1981, and again in 1991, in the USA of six bridge decks that had been subjected to de-icing salts and one bridge in Florida with seawater exposure [2,52]. This work was undertaken to compare the performance of galvanized and uncoated reinforcement in decks exposed to de-icing salts in winter or year round to humid marine conditions. After periods up to 24 years exposure it was found that the galvanized bars had suffered only superficial corrosion in sound, uncracked concrete, even when the chloride levels were high. The remaining zinc thickness was high enough to guarantee further long-time protection In 2002 a study of two bridges nearly 30 years old was undertaken with a positive result concerning galvanized reinforcement. In some cases also the chloride concentration at the level of the galvanized bars was measured [52]:

- 0.26-0.40 % by weight of cement (Boca Chica Bridge, Florida, 19 years),
- 0.04-0.71 % by weight of cement (Ames Bridge, Iowa, 24 years),
- 0.08-0.75 % by weight of cement (Athens Bridge, Pennsylvania, 18 years)
  average 0.41 % by weight of cement (Athens Bridge, Pennsylvania, 28 years),
- 0.16-0.89 % by weight of cement (Coraopolis Bridge, Pennsylvania, 19 years),
- up to 1.45 % by weight of cement (Tioga Bridge, Pennsylvania, 17 years)
  average 0.40 % by weight of cement (Tioga Bridge, Pennsylvania, 17 years).

From the reinforcement corrosion point of view however, these chloride contents are not so high that strong corrosion has to be feared if non-galvanized and galvanized steels are embedded in the concrete of the mentioned structures.

Together, these bridge deck studies, and the 237 bridge deck evaluations conducted by the Pennsylvania Department of Transportation, have uncovered only one area of deck distress (Bradford County). The single incident may be characterised as resulting from defective concrete, permitting extraordinary high levels of chloride concentration. There were no failures of the galvanized reinforcing bar performances in decks constructed in accordance with standard specifications.

In spite of these encouraging results of the performance of galvanized reinforcement, the USA Federal Highway Administration did not recommend galvanizing for general application in bridge decks. This was due to some poor laboratory results showing premature failure. But after nearly four years further laboratory testing in the USA and Canada, the poor results have yet to be confirmed. This has led to some controversy.

Among bridges in oceanic environment, three bridges extremely exposed to spray of seawater were inspected respectively after 3, 8 and 21 years of service [50]. Ribbed bars with average zinc coating thickness 130 to 250 µm were used. The concrete had a water/cement-ratio of about 0.44. With proper compaction, such a concrete is usually regarded as sufficiently resistant against intrusion of chlorides. The chloride content in % by weight of cement at the reinforcement and the amount of lost coating were measured, and the results were:

bridge	**age** [years]	**cover** [cm]	**chlorides** [mass-%]	**zinc loss** [µm]
1	3	3.8	0.56	5
2	8	5.7	0.25	5
3	21	5.7	0.45	50 - 100

In another bridge with much the same environment, the 28.5 cm thick concrete deck had chloride content of 0.4 - 0.7 % at the reinforcement after 3 years. In areas with non-galvanized reinforcement there was a marked corrosion with cracks in the 3.2 to 7.6 cm cover. In areas with zinc-coated reinforcement, the 190 µm coating showed nearly no attack.

Inspection of four structures exposed for several years in the tidal zone, gave as result [51]:

structure	**age** [years]	**cover** [cm]	**chlorides** [mass-%]	**zinc loss** [µm]
1	7	13.2	1.4	2
1	10	6.2	2.2	5
1	12	8.0	2.7	13
2	8	7.4	1.6	< 2
3	10	5.4	0.8	5
3	10	6.8	1.4	4
4	23	10.5	1.9	5

The chloride content was larger than for structures intermittently wetted. In spite of all the chloride, the loss of zinc was very little compared to the original coating thickness of 100 - 200 µm. Only in the case of poor quality concrete (holes and pores) in structure 1, with original coating thickness of 100 - 160 µm, a complete loss of zinc was found after 7 years exposure.

In another case [49], galvanized bars with cover of 30 - 90 mm were mostly intact after 12 years exposure in the tidal zone.

There are further examples of applications with galvanized reinforcements in North America, Europe, Australia and Japan also in contact with seawater or atmospheric conditions (e.g. thin-walled structures and cladding panels) [2]. The structures were mostly intact after some to 20 years in service and the reports give the impression of successful results. However, it is mentioned shortly: “There are other structures in North America where galvanized reinforcement has not performed well and have required costly maintenance programmes.” It is a pity that no further details are reported. Could the reason be that the works were not carried out according to specifications? In any case it leaves an open question mark as to the effect of galvanized reinforcement.

3.6 Benefits from the use of galvanized reinforcement

As to the benefits from the practical use of galvanized reinforcement, this report lists the following points:

- Proper galvanizing procedures have no significant effect on the mechanical properties of the steel reinforcement.

- The bond behaviour of galvanized bars is, if anything, better than of non-galvanized ones. There seems to be no negative influence on bond of galvanized reinforcement, if chromate reduced cements are used.

- Corrosion of galvanized steel in concrete is less intense and extensive for substantial period of time than that of non-galvanized steel. Galvanizing delays the onset of cracking, and spalling of concrete is less likely to occur or is delayed.

- Galvanized steel rebars are particularly suitable as reinforcements in concrete structures subjected to carbonation, and in this case the extension in their corrosion life can very easily exceed 40-60 years. Therefore, galvanizing may be recommended, e.g. for reinforcements in precast and also thin-walled elements, in lightweight and porous concrete structures in contact with the atmosphere.

- Galvanized reinforcements tolerate a higher concentration of chloride ions than do non-galvanized steel bars (about 2-3 times). The extension of service life in this case depends on many factors, including the type of cement, concrete mix proportions, quality and thickness of the pure zinc layer and the humidity content of the concrete.

- Greater chloride-compatibility is obtained with low alkali cement. The relation between alkali content and corrosion rate might help to solve the controversy regarding the stability of galvanized reinforcement in chloride-contaminated concrete. It may explain the fact that as most North American cements have low alkali contents, galvanized reinforcements has been mostly successful there.

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4 Epoxy-coated reinforcement [1-7]

Organic coatings to the reinforcement are almost exclusively based on epoxy-resin powder coatings. Epoxy resins free from pores, cracks and damaged areas perform well in terms of corrosion protection, adhesion, mechanical stability and resistance to alkaline environments. Epoxy-resin coated reinforcement has been in use for over 30 years, particularly in North America [8].

In contrast, 20 years ago a trend in Germany was to use epoxy coating for the protection of bars, but to use polyvinylchloride- (PVC-) coating for welded wire fabric, because of the need for a more ductile (even though weaker) material for coating the fabric. This development was not successful [9] and PVC-coatings for protection of steel for concrete application disappeared from the market. The coating material was not sufficiently resistant in the alkaline medium of the pore water. The reason was a plasticizer migration out of the PVC and a saponification as a result of a reaction between plasticizer and the alkalinity of the concrete pore water. As a consequence the material embrittled, cracked and under-rusting took place within a very short time of few months. Already very early, it was found that polyvinylchloride coated bars developed less than acceptable bond strength in concrete, and therefore should not be used as reinforcement e.g. in bridge decks [10].

4.1 Manufacture of the coating [7]

The application of an epoxy coating can be performed in different ways:

- Using liquid epoxy which is brushed or sprayed on the steel, or the steel is immersed into the liquid epoxy. Liquid epoxy contains solvents that evaporate after application, resulting in pore formation. In addition liquid coatings shrink, and prior to hardening the coating material flows from the top of the ribs, resulting in a thin coating at the top of the ribs while the coating layer may be quite thick between them.

- Preheated steel is passing a fluidized bed with epoxy powder which fuses to the steel surface. Air is either passed through the bed of coating powder so that the powder behaves like a fluid, or the steel passes just over electrically charged powder which is attracted to it.

- Electrostatic spraying of epoxy powder to the steel. Electrostatic spraying of straight lengths of rebar currently accounts for the majority of coated rebar. In electrostatic spraying after cleaning the steel by abrasive blasting, the electrically charged powder particles are sprayed onto a preheated steel surface (+230 °C) where they melt to form an even and uniform powder film. After a heat catalysed irreversible reaction, the powder starts to gel. After the film is solidified the coated bars are cooled in water or air. As a result a uniform coating without pores and cracks is the best. Experiences showed that fusion bonded epoxy-coatings render rather even thicknesses, even across the ribs on ribbed bars.

Because of better performance and better corrosion protection efficiency electrostatic spraying of epoxy powder to the straight lengths of rebar currently accounts for the majority of coated rebar [10,11]. The report therefore concentrates on the last method of electrostatic spraying. With regard to failures in application of epoxy-coated bars in sub-structure of marine bridges, some producer use chromated bars to improve adhesion between steel and epoxy.

The protection against penetrating of corrosive agents between the steel substrate and the coating depends of a good bond to the steel surface. Correct steel preparation done by abrasive blast cleaning and pre-treatment (chromating or others) is essential, particularly ensuring no contamination with chlorides or other aggressive ions. The best adhesion is obtained from steel which has been blast cleaned to Sa 2 ½ (no residual scale, rust or coating).

4.2 Properties of the coating and of epoxy-coated reinforcement [3,7,10,12,13]

In order to protect the reinforcement against corrosion in concrete, the required properties of the epoxy powder and the coating are:

- The powder of organic composition shall form a film free from holes, voids, cracks, contamination, damaged areas and holidays. The reinforcing bars shall be uniformly coated over ridges and valleys with small deviations in coating thickness.
- A good adhesion of the coating to the steel surface is necessary otherwise under-rusting may occur.
- Chemical resistance against the alkaline environment of concrete, against carbonated concrete, water and salty aqueous solutions. The coating must then not blister, soften, lose bond, nor develop holidays.
- High resistance against low (freeze) and elevated temperatures (heat of hydration).
- High diffusion impermeability against water vapour and oxygen as well as sufficient chloride impermeability.
- High bond strength to concrete and high resistance against slippage between the coated bar and the embedding concrete under load.
- Good mechanical properties such as good formability, impact resistance and abrasion resistance. As most bars are coated in straight length it is essential that the coated bar can be bent without cracking/rupture of the epoxy coating on the exterior side of the bent bar.

For these reasons epoxy coatings are extensively investigated in laboratory tests (e.g. [14]), not always meaningful interpreted with regard to the practical circumstances.

Experience to date has shown that it can be taken for granted that a correct steel preparation in connection with a suitable and defect free epoxy coating mostly fulfil these conditions. The flexibility of the coating and the bond to concrete depends upon its binder properties and its thickness. The thinner the layer, the more flexible the coating and the better the bond. However, if it is too thin its ability to protect against corrosion decreases.

4.2.1 General properties

Owing to their chemical composition, epoxy resin exhibits several mechanical/physical properties such as high ductility, small shrinkage in polymerisation, good abrasion resistance and good heat resistance up to moderate increased temperatures. It has an excellent adhesion to a well pre-treated steel reinforcement, ensuring no delamination as a result of corrosion forces. Epoxy coatings show good mechanical resistance against abrasion, and a good flexibility if the thickness is not too great.

However, there exist some possible problems with application of epoxy-coated reinforcing steel:

- This coating is more fragile than a metallic coating. Epoxy-coated reinforcement must therefore be handled with more care during storing, transport and handling on site than untreated steel bar reinforcements as the coating may be damaged if roughly handled. They should be protected against impact and bar-to-bar abrasion must be prevented. The experience clearly indicates that a certain amount of damage can occur during storage, transport, site handling, steel fixing and compacting concrete.

- The preferred procedure of coating plants is to coat straight bars and then to fabricate them. Coated bars are normally bent and cut at the site. The coating may break at the tension section during bending.

- Cutting points and cracks caused by bending as well as other coating defects formed during careless handling have to be repaired using liquid epoxy. It is advisable to patch only the major defects which cause a corrosion risk. The ASTM standard requires that the maximum amount of damaged areas on a bar shall not exceed 6 per metre or 2 % of the surface of each bar. The requirements for a good repair make it doubtful that this is achievable on site. Further repaired areas may suffer preferential corrosion attack in concrete structures exposed to aggressive environments [15]. In field tests the corrosion had spread from the repaired area under the powder epoxy coating.

- The performance of coated steel may be also adversely affected by the damage occurring during concreting. Such damages cannot be repaired.

4.2.2 Durability of the coating

Epoxy coating is characterised by its resistance to alkaline medium with no softening or peeling off. Epoxy resins normally exhibit good durability against solvents, chemicals and water. The long-term durability of most epoxy-coatings in concrete is good. They will not soften or deteriorate in the highly alkaline environment.

4.2.3 Protection properties

The purpose of the coating is to isolate and insulate the steel from the corrosive environment. Coating thickness is important. Thin epoxy coatings up to 250 μm are not completely impermeable to oxygen and moisture, but diffusion can be reduced by sufficient thickness and density. The epoxy resins are very impermeable to chloride ions. Chloride permeability in a defect free coating is considerably lower than that of water vapour and oxygen if a powder epoxy coating has a thickness of 130 - 250 μm [11]. However, the epoxy-film is not completely free of pores after coating. Consequently, for optimal corrosion protection a thick coating is desirable. But considering bond between coating and steel and bond between coated bars and concrete, large thickness are unfavourable. The usual range of coating thickness required to fulfil flexibility, bonding and corrosion protection requirements is between 130 and 300 μm. This thickness of epoxy powder coating is also recommended in US standard ASTM A 775-81. Experience indicates that the optimum balance between coating flexibility and corrosion protection is reached at circa 200 μm.

Epoxy-coatings are regarded as providing better protection against high chloride concentrations than hot dip galvanizing. This is proven when comparing investigations on different corrosion protection methods (chapter 4.4.1) [16].

4.2.4 Mechanical properties of the steel

No special influences on the properties of the steel is either reported or known.

4.2.5 Fatigue behaviour of the steel

Reinforced concrete structures are often subjected to cyclic loads in combination with corrosive attack which may result in corrosion-fatigue damage. To assess the corrosion assisted decrease of the fatigue-limit of reinforced concrete structures beams with uncoated and corrosion protected reinforcement exposed to a critical environment (e.g. seawater) were tested. Seawater exposure simulating splash-zone or submerged conditions lowers considerably the fatigue amplitudes of unprotected steel. By using additional corrosion protection methods, e.g. by epoxy coating or galvanizing, it may be possible to avoid the critical decrease of fatigue strength of existing structures. It was found from tests in seawater that epoxy coating is superior to galvanizing [17,18]. In other tests, beams were tested with a low frequency of 0.5 s^{-1} cyclic bending load in seawater [14]. In these long-time tests epoxy coating did not improve the corrosion fatigue behaviour of the bars. The coating wore out in areas of concrete cracks. This can be attributed to fretting between epoxy and concrete. This led to local underfilm rusting and scale off the coating.

4.2.6 Weldability

Welding of coated bars may generate noxious fumes from the resin. Measures should therefore be taken to ensure the safety of the working environment. In gas-pressure welded joints, if the end surface and periphery of the weld are coated with epoxy-resin, the surface of the weld will not be in close contact, being left as a flat fracture. Therefore, the coating on the end surface to be welded must be completely removed prior to the welding.

4.2.7 Bond behaviour

Experience with synthetic resin-concrete bond behaviour, considering the influence of bar size, concrete strength, epoxy coating thickness, load and time on bond, showed care must be exercised when coated reinforcement is used in structural application.

With respect to polyvinylchloride, it was found that coated bars develop less than acceptable bond strength in concrete, and therefore should not be used as reinforcement, e.g. in bridge decks [10,12,19].

According to several studies on the base of pull-out test, creep-test and repeated bend load, pulling test bars from test bodies of concrete, epoxy coating also has a smoothing effect on the surface configuration of indented bars. Epoxy coating has the effect of significantly reducing bond resistance and increasing slippage between reinforcing bars and the embedding concrete in comparison to uncoated bars [10,11,19,20-25]. The thicker the coating is, the greater is this effect. Coated bars with film thickness larger than 500 µm are very disadvantageous for the bond behaviour [10], thicknesses smaller than 250 µm have comparable bond strength to, but higher slip than, uncoated bars [10,11,21].

Bond to concrete may be defined either as the ultimate stress at pull out, or as a certain slip between bar and concrete at lower stress. Bond stress is defined as the axial force developed in the reinforcing bar divided by the nominal surface area of the bar in the anchorage length.

With respect to the ultimate bond stress, it seems that the epoxy coating reduces strongly the adhesive bond to concrete. Plain bars, and those with relatively shallow ribs have demonstrated large reductions in bond when epoxy-coated. It seems that one has to rely on the mechanical bond caused by the ribs. The effective rib height of coated bars seems to be the original rib height minus the coating thickness on the core of the bar. Due to the smaller rib heights on the thinner bars, the percentage reduction in the rib area will be larger than that for greater bar sizes. Consequently, at a constant coating thickness a more pronounced reduction in bond should be expected at smaller bar sizes.

Coating thickness larger than 500 µm decreases the bond distinctly [10]. If the thickness is 300 µm or below, the bond values are similar to those of uncoated bars.

The effect of bond strength can be quite sensitive to bar diameter depending upon type of bar and of test. At pullout failure, reductions up to 20 % are reported [23,24] in more normal cases. The reduction would appear to become smaller as the bar diameter is increased. However, the geometry of the deformation can be very important and affect the pull out strength of epoxy coated reinforcing bars [22]. At splitting failure the bond was about 65 % of uncoated bars. In another study on bond epoxy-coated reinforcing steel developed only 66 % of the bond stress of uncoated bars [25].

Regarding slip of epoxy-coated bars, some tests demonstrate a larger slip at lower loads. But the total slip at ultimate load seems to be roughly the same as with uncoated bars.

The width and spacing of concrete cracks was increased by epoxy coating. Beam tests exhibited in the average about 50 % increase in concrete crack width when the bars were epoxy-coated, but the beam stiffness measured by deflections was not affected [19,23,24]. In single cases the average width of cracks was nearly twice the width of specimens with uncoated bars.

Fig. 4.1 compares the bond behaviour of ribbed uncoated and epoxy- respectively PVC-coated bars, diameter 16 mm, in pull-out test. If the slip is low, plastic coatings reduce strongly the adhesive bond to concrete in comparison to uncoated bars. However, the harder epoxy-coatings have advantages compared to the weaker PVC-coatings. The enlarged softness causes a greater reduction in the reinforcement to concrete bond. If the slips are higher the shearing bond of the coated ribbed bars becomes better and there is no difference between epoxy-coated and uncoated steel. With a so-called rough coating developed in Germany [13], the loss of adhesion bond of epoxy-coated bars is excluded.

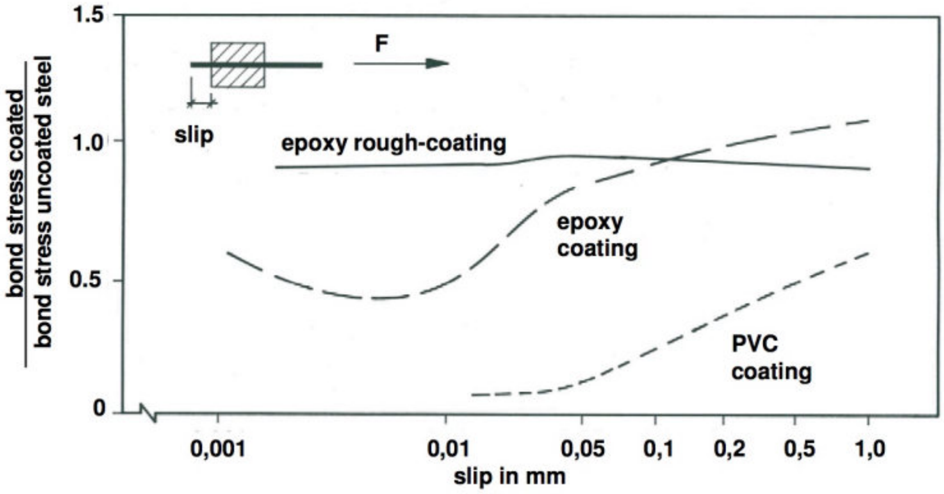

Fig. 4.1: Comparison of the bond behaviour of coated and non-coated bars [13]

Based upon the afore-mentioned results concerning reduction of bond stress and increasing of concrete cracks by epoxy coating, the rules in USA for development length of epoxy-coated bars were discussed. Compared to uncoated bars, the requirements are likely to be [3]:

- 50 % increase in tension development length when the concrete cover is less than the bar diameters or when clear spacing between bars is less than six bar diameters. The intent is to control potential splitting failures through the cover, or splitting between bars in one layer.
- 20 % increase for all other conditions of cover and bar spacing.
- The combined factor (increase) for top bar effect and epoxy coating does not have to exceed 1.7.

The British Cement Association reported in December 1990 the results of a series of bond tests which compared uncoated and epoxy-coated bars [22]. The overall conclusions of these tests, when comparing fusion-bonded epoxy-coated reinforcement with uncoated, are:

- There is a 20 % reduction in the bond capacity for bottom cast epoxy-coated bars.
- For top cast bars there is no significant difference in the bond capacity.
- Lap length of epoxy-coated bars in tension should be increased by 25 % in the bottom cast position. (It is likely that tension laps in the top cast position need not be altered.)
- There is no significant difference in the shear capacity.

Also the bond to concrete under repeated loading was tested [3]. Under bond fatigue loading in working stress range, the slip of uncoated bars covered with mill scale, epoxy-coated bars and uncoated sandblasted bars was essentially the same. After the first load cycles, epoxy-coated bars showed larger slips at the loaded end than mill scale bars. The difference in loaded end slip usually diminished somewhat as the number of cycles increased. The bond strength of epoxy-coated bars compared to mill scale bars is not adversely affected by up to 1.4 million cycles of loading in the serviceability stress range.

4.2.8 Extreme temperatures [3]

Epoxy-coatings lose their stability at temperatures of about 200 °C. The bond between epoxy and concrete may be affected by softening and melting of the coating. Pull-out tests were carried out at temperatures from 110 to 370 °C. Both uncoated and coated 19 mm ribbed bars were used. The uncoated bars withstood 20 % greater pull out loads. However, the test showed that epoxy-coated bars heated to these temperatures developed stresses greater than their nominal yield stress (which is temperature dependent) without pulling out.

In this test, displacements were measured at maximum load both at the free end and at the loaded end. The total displacement reported includes both those caused by slip and those by elastic and inelastic elongation of the bar. For uncoated bars, displacement at free end was generally zero. For epoxy-coated bars it was more significant. Up to 150 °C, displacements at the free and loaded ends were almost of the same magnitude. This indicates that pull out of the epoxy-coated bars may be caused by softening or melting of the coating. At temperatures of 260 to 370 °C, displacements of epoxy-coated bars at the free end were about half of that of the loaded end. This does not necessarily indicate pull out, but it does indicate some bar slip.

4.3 Current specification

Standards for epoxy-coating reinforcing steel cover testing in the laboratory and the application in practice.

Existing international standards:

- ISO 14654, Epoxy-coated steel for the reinforcement of concrete; International Organization for Standardization (1999),

  specifies requirements for fusion-bonded epoxy-coated post-fabricated and pre-fabricated steel bar, wire and welded fabric for the reinforced concrete. It permits the application of either flexible (type A) and nonflexible (type B) coatings. Steel reinforcing bar, wire and welded fabric coated with a nonflexible (type B) coating shall not be fabricated after coating.

- ISO 14656, Epoxy powder and sealing material for the coating of steel for the reinforcement of concrete; International Organization for Standardization (1999),

  specifies requirements for epoxy powders for use in preparing fusion-bonded epoxy-coated steel reinforcing bar, wire and welded fabric. This standard also includes requirements for sealing material used to repair damaged areas and cut ends on reinforcing steel.

Further some national standards exist, as in the USA:

- ASTM A 775/A 775M-97 Standard Specification for Epoxy-Coated Reinforcing Steel Bars; American Society for Testing and Materials (1997),

- ASTM A 934/A 934M-97 Standard Specification for Epoxy-Coated Prefabricated Steel Reinforcing Bars; American Society for Testing and Materials (1997),

- ASTM D 3963/A 3963M-97 Standard Specification for Fabrication and Jobsite Handling of Epoxy-Coated Reinforcing Steel Bars; American Society for Testing and Materials (1997),

and in Switzerland:

- ASTRA-Richtlinie zur Anwendung von epoxidharzbeschichteten Betonstählen. Bundesamt für Strassenbau, Switzerland (1991).

These standards specify

- identification of the coating material, water vapour transmission and water absorption and durability of the coating (ASTRA),

- substrate treatment (ISO 14654, ASTM A775, ASTRA),

- absence of porosity (ISO 14654, ASTM A775 and A934, ASTRA),

- coating thickness and coating thickness measurement (ISO 14654, ASTM A775 and A934, ASTRA),

- bending capacity measurement (ISO 14654, ASTM A775 and A934, ASTRA),

- alkali resistance (ISO 14654, ASTM A775 and D3963, ASTRA),
- salt-spray test (ISO 14654, ASTM A775 and D3963, ASTRA).

In ISO 14654 the requirements for the epoxy-coated steel are prescribed. ISO 14656 defines the requirements to the coating powder and the sealing material. These demands correspond to the test programme in ASTM A775. According to the afore-mentioned standards, the finished coating thickness shall be at least 170 and 175 µm. respectively. There shall be not more than 3 to 4 holidays (pinholes not discernible to unaided eye) per metre of bar. The adhesion of the coating to the steel is tested by bending coated bars 120° around a mandrel with diameter 8 to 10 times (ASTM) respectively to an angle of 180° around a mandrel with a diameter 4 to 6 times (ISO) that of the bar without cracking or debonding appearing in the coating on the outside of the bend. The bond stress reduction should no exceed 15% when compared with uncoated steel (ASTM A775).

4.4 Corrosion protection behaviour

4.4.1 Results of laboratory and field tests

The purpose of the coating is to isolate and insulate the steel from the corrosive environment. The coating acts solely as a barrier against the environment. It was found that the cured films of the powder epoxies were essentially impervious to chloride ions over a long time [10]. However, as described by certain literature [11,26] none of the investigated coatings are totally impermeable. All are pervious, not only to water but to a slight degree also to chloride ions. More variable results were obtained with the cured films of liquid epoxies.

The epoxy-coatings used today to protect reinforcing steel contain no corrosion inhibitive pigments. To provide adequate protection, the coatings should have a minimum thickness. Nevertheless it should not be so thick that it impedes flexibility and bonding of the coating between steel surface and concrete. If there are defects on the coating through which aggressive agents can penetrate the barrier, corrosion concentrates on these areas. Integrity of the coating therefore is essential for effective corrosion protection. The film must therefore be free from pores, cracks and damaged areas.

The corrosion performance of epoxy-coated rebar was the subject of extensive laboratory and field tests, which began in the early 1970s. In numerous accelerated corrosion tests, natural exposed epoxy-coated, untreated or alternatively protected steel bar reinforcement have been compared [11,26-34]. Nearly all reported laboratory tests or practical experiences include the effects of chlorides.

Laboratory tests generally suggested that epoxy coating provides good corrosion protection. It was therefore concluded that the use of epoxy-coatings, free of essential defects, guarantees considerable long-term protection to the steel in carbonated concrete and a significant reduction in the rate of deterioration of reinforced concrete containing high levels of chloride. The corrosion prevention ability of liquid epoxy-coatings is not quite as good as that of powder epoxy-coatings. Liquid coatings may have many holidays or are more permeable to water and/or chloride ions [11].

However, the use of coatings in chloride containing concrete does not provide complete protection [16,29] (see also chapter 4.4.2). Corrosion of the steel may be initiated at breaks in the film. In concrete with high levels of chloride an attack was observed to be spreading from points of defects in the coating. There was very little bonding between the steel and the coating. Film debonding appears to be a consequence of cathodically controlled underfilm corrosion [29]. This caused a systematic breakdown of the coating and cracking of concrete. These results indicate that epoxy barrier coatings may have a finite tolerance limit for chlorides.

Table 4.1 shows typical results of extensive investigations of reinforced concrete beams partly dipped in saturated chloride solution [27]. 100 beams were reinforced with unprotected steel, 100 beams with epoxy-coated steel according to US-specification ASTM A 775 (< 6 defects/m, sum of defects < 2 %) and 100 beams were reinforced with epoxy-coated steel with a greater number of defects in the film, as designed. The criterion for the judgement of the corrosion behaviour was the corrosion assisted cracking of the concrete specimens. These results show clearly the advantage of the coating with respect to steel protection but also the detrimental influence of defects on the protection efficiency of epoxy coatings.

Table 4.1: Number of concrete specimens with cracks depending on time [27]

kind of reinforcement	**concrete cracks after ...... months**						
	20	25	34	45	52	70	80
unprotected steel	17	42	100	100	100	100	100
epoxy-coated steel according to US specification	0	0	0	0	0	3	5
epoxy-coated steel not according to US specification	0	0	0	0	3	26	49

It is therefore very important to avoid damage to the coating, such that the underlying steel is not exposed. Should damage occur, and should that damage be sufficiently large, the corrosion of the underlying steel can be more extensive (chapter 4.4.3). Repairing defects with repair epoxy does not improve the corrosion protection significantly. Investigations carried out by [15] have shown that repaired areas had suffered corrosion after three years embedment in chloride containing concrete.

Subsequently some further detailed information about test results is given regarding the use of epoxy-coated reinforcement in bridge decks exposed to de-icing salts. Many tests therefore relate to bridges. A field study by the Pennsylvania Department of Transport of 'Bridge Deck Protection Measure' [31,32] included half-cell and electric-resistance field determinations, chloride and permeability measurements, and visual inspections of reinforcing bars in cored samples off 22 bridge decks. Although there were some mixed results in the comparative evaluations, the overall consensus from the work was:

- Coated reinforcing bars should prove to be more effective in corrosion protection than low-slump concrete, latex-modified concrete, membrane or overlay systems.
  (The validity of this result must be questioned or relativized knowing that US bridge decks have normally no membranes or overlay systems).

- Under short-term exposure (less than 35 years), galvanizing and epoxy-coating should be equally effective in corrosion protection.

- Zinc coating is sacrificed during the short term, and therefore epoxy-coating should be more effective if longer-term protection in chloride enriched concrete is required.

- Lack of adhesion between the concrete and the epoxy-coated reinforcement emphasises the importance of mechanical interlock in the bond strength of epoxy-coated reinforcing bars.

When fusion bonded epoxy coated reinforcement became available in the UK an exposure trial was undertaken to evaluate the performance of this material [29]. Epoxy coating has been subjected to accelerated testing on a natural exposure site over a 5-year period alongside plain steel and galvanized steel in purpose-designed concrete specimens.

Findings of this programme of research were that epoxy-coated reinforcement provided considerable protection to the steel for the length of the trial when exposed in concrete with a high concentration of added chloride, leading to significant practical advantage. However, the use of these coatings in practice does not provide complete protection since corrosion was observed to be spreading from points of defect in the coating when the steel was embedded in concrete containing high levels of chloride. Damage to the coating at bends or cut ends may reduce the durability of the material. This means that integrity of the coating is essential for effective corrosion protection and coated bars therefore must be handled with greater care than uncoated bars. Defect-free epoxy-coated reinforcement in chloride enriched concrete offered enhanced reinforcement durability relative to galvanized or unprotected carbon steels.

An accelerated corrosion test from Japan [6,28] involved both uncoated bars and bars with epoxy-coating thickness of 100, 200 and 300 μm. The concrete cover was 20, 40 or 70 mm. The percentage of corroded area of the total steel surface inside specimens cured in the tidal zone was measured. According to the concrete cover the uncoated bars showed more or less corrosion from 1 year onwards. All epoxy-coated bars remained totally free from corrosion regardless thickness of cover or of coating and the length of curing time (till 3 years). The coating also had retained its initial properties of hardness, glossiness, adhesion to steel surface and continuity.

Finnish tests [11,26] including more than 300 cylinders with embedded bars, investigated how different curing conditions influence the durability of coated bars. Their conclusions were:

- Sound epoxy coating gave good protection against corrosion even in aggressive environment. Coated bars were in good condition after 24 and 36 months of seawater curing inside cracked concrete cylinders containing $CaCl_2$.

- Coating with damages considerably weakened the corrosion prevention.

- $CaCl_2$-addition increased the corrosion of bars with damages in coating.

- Cracks in the concrete did not increase corrosion.

- Seawater curing increased steel corrosion remarkably.

All coating materials had a certain permeability in relation to their thickness. The Finnish report mentions that epoxy-coatings absorb water to some extent. Hence thin coatings (50 - 250 μm) are not totally impermeable to water. Chloride permeability is considerably lower than that of clean water. Test results indicate the chloride ion permeability of powder epoxy-coatings to be zero, or very much less than that of liquid epoxy-coatings.

During 7-year exposure period in the environment of Eastern Saudi Arabia the following results have been gained on unprotected mild steel, galvanized, epoxy-coated and stainless clad reinforcing steels in chloride containing specimens of good-quality concrete containing three levels of chloride (0.6, 1.2 and 4,8 % by weight of cement) [21]:

- Uncoated mild steel had suffered severe rust-related damage for all three chloride levels with significant loss of section.

- In the case of galvanized reinforcing steel in equivalent chloride-bearing concrete, compared to bare mild steel, there was a delay in the onset of cracking, a reduction in metal loss and an amelioration in the incidence and severity of concrete failure condition. However, in both 1.2 and 4.8 % concretes, there has been severe corrosion accompanied by concrete cracking. The results indicate that the use of galvanized steel in concretes with high levels of chloride merely delays concrete failure by only a finite period of time.

- Epoxy-coated bars performed exceedingly well as corrosion-resistant steel in 0.6 and 1.2 % chloride concretes, as no corrosion and concrete cracking were observed. However for the 4.8 % chloride concrete, significant corrosion was observed on the substrate steel under the coating. This caused a systematic breakdown of the coating and cracking of concrete. These results indicate that epoxy barrier coatings may have a finite acceptance limit for chlorides.

- Among corrosion-resisting steels, the best durability performance was exhibited by stainless-clad reinforcing bars. After 7 years of embedment in 4.8 % chloride concrete, no sign of corrosion was observed on many of the bars tested.

4.4.2 Cracks in concrete

In [3] tests are reported which showed that cracks in the concrete did not increase corrosion of epoxy-coated bars with an undamaged coating. It was concluded that the epoxy-coated reinforcement greatly reduces the incidence and extent of corrosion in cracked structural members. However, it is also reported (chapter 5.5.2) that if the corrosion protection is restricted in uncracked concrete this reduction is valid, particularly in the area of cracks.

The investigations were conducted in that way that a salt solution was ponded on the top surface of cracked concrete specimens reinforced with unprotected and epoxy-coated reinforcement. After some time on uncoated bars heavy corrosion (severe pitting) was observed on a majority of the specimens. This was quite the opposite for epoxy-coated bars which showed very little corrosion until crack widths of some tenths of a millimetre were reached.

4.4.3 Defects/cracks in the epoxy-coating, resistance to galvanic corrosion

Coating failures are generally governed by the following models:

- Aggressive agents can penetrate through defects in the coating, down to the steel surface. Corrosion concentrates on these areas, resulting in reduction locally of the bars cross sectional area. Small defects are not regarded as causing any corrosion risk. Only larger defects are required to be patched.

- Starting from local defects, a process like crevice corrosion beyond the coating may also take place. As chlorides diffuse between substrate and coating, voluminous corrosion products form, which lift the coating in the area around the defect (Fig. 4.2). However, the bond of epoxy coating to the steel is normally too good for any undermining of large areas to take place. Should undermining occur, the corrosion between coating and steel often results in formation of flat cavities where there is little oxygen, and the corrosion process therefore is slow.

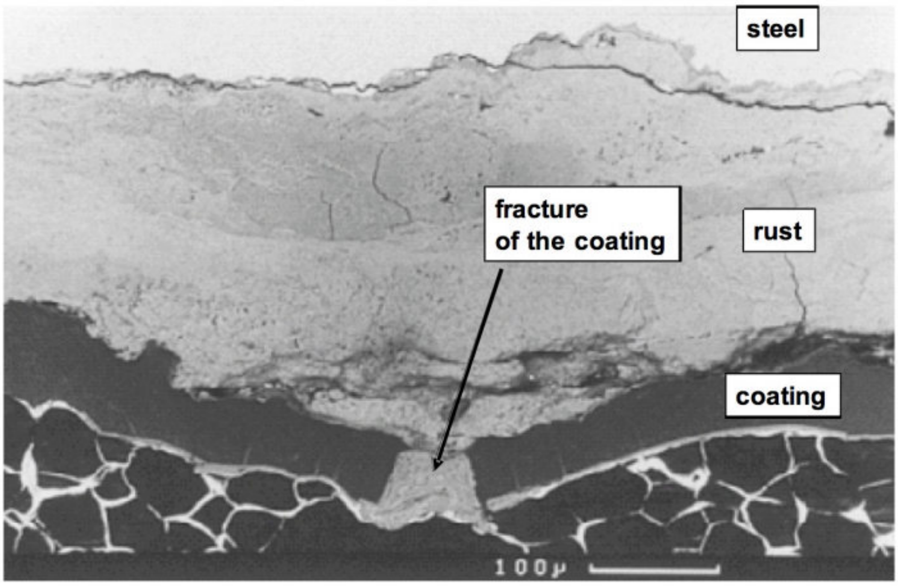

Fig 4.2: Under-rusting of a PVC-coating starting from local defects

- With respect to macrocell corrosion at damaged/cracked areas of coated bars, this type of locally intensified attack may be favoured in the presence of water, dissolved chlorides and increased temperatures. The defects/cracks can serve as anodes and the undamaged epoxy coating situated close to anodic areas can act as cathode if the following preconditions are fulfilled [1]:
  - The wet coating has a high electrolytical conductivity.
  - A high oxygen permeability of a low coating thickness guarantees that areas beyond the coating can act as cathodes of corrosion elements, especially if adhesion is removed. If the cathodic half-cell reaction proceeds, this reaction produces localized pH values high enough to trigger cathodic adhesion loss in the coating at these locations, weakening anti-corrosion performance still further.
  - At the damaged area (anodes), access of chloride ions leads to high concentrations.

The relation between cathodic and anodic areas will then govern the situation. As this ratio usually will be small, the rate of corrosion will also will be minimal. However, the similarity between the anodic laboratory behaviour and the field corrosion morphology [35] suggested that the damage at bridges (see below) may have taken place at the anodic end of corrosion macrocell, which could be active in marine substructures [15,36].

The use of coated bars in only the top mat of reinforcement was standard practice in USA and Canada throughout most of the 1980s. Today both layers are usually coated. However, the question arises whether there is a danger of macrocells developing between coated and uncoated steel in similar application [37]. Fig. 4.3 shows a small anode formed in a coating defect on the top reinforcement of a parking deck, while the entire bottom reinforcement acts as a cathode. If there is a conductive connection between the coated and uncoated reinforcement, there is a danger of cell formation if the following conditions exist (see also above):

- existence of active (anode) and passive (cathodic) surface areas,
- electrical and electrolytical connection (conductivity) between anode and cathode,
- existence of oxygen in the cathodic area.

The conditions are especially unfavourable if the coated steel with small defects (anodes) in the coating is embedded in humid (badly aerated), chloride containing concrete and the uncoated steel (extensive cathode) is in dryer (well aerated) still passivating concrete [2,6]. Then sufficiently high differences of potential arise. High current densities may develop in the area of local faults, i.e. when small anodes are opposed to extensive cathodes.

With respect to macrocell corrosion in connection with the application of epoxy-coated reinforcement extensive field tests are reported from FHWA (USA) [31]. In these investigations two layers of reinforcement have been embedded: an upper layer in chloride containing concrete (0.4 % by weight of concrete) and a lower layer in chloride free concrete. Three different cases have been compared in the reinforced bays of good concrete quality:

a) both reinforcing layers uncoated,

b) both layers coated and with damages,

c) upper layer coated and with damages, lower layer uncoated (Fig. 4.3).

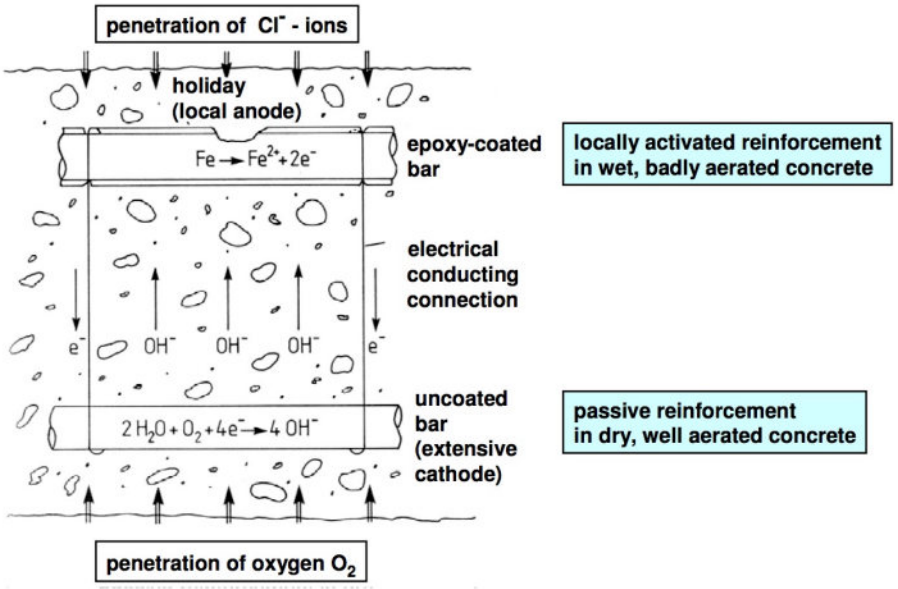

Fig. 4.3: Corrosion cell between epoxy-coated bar and uncoated reinforcement (e.g. parking decks) [1]

Both reinforcement layers were connected so as to be electrically conductive. Case a) (connection of uncoated steels) showed the highest corrosion currents. However, regarding the currents measured at the real anodic surface (Fig. 4.4) case c) gives a ten times higher corrosion current density than case a) because in case c) only 1 % of the surface acted as anode. It follows that by using coated reinforcement the formation of macrocells should be considered.

4.5 Practical experiences with application

4.5.1 Extent of use

The first major field application of epoxy-coated reinforcing bars was in a Pennsylvania bridge deck in 1973. Fusion bonded epoxy-coated reinforcement reached the commercial market in 1976, and fusion bonded epoxy-coated welded fabric in 1984.

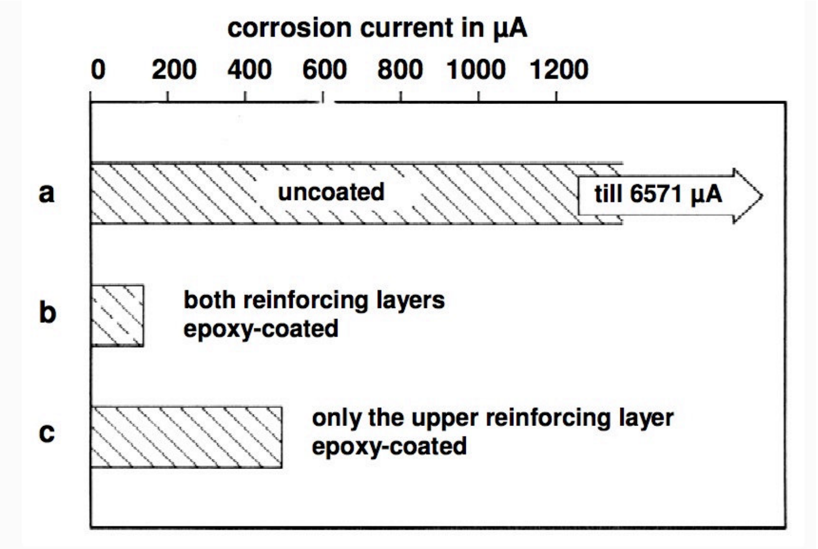

Fig. 4.4: Corrosion currents depending on the state of coating (FHWA)

Today epoxy coating is one of the most widely used techniques for protecting reinforcing bars against corrosion inside the concrete. The effectiveness of epoxy coating as a corrosion prevention method was first studied in the USA and Japan [3,6]. This method later spread also to Canada, the Middle East and Europe. Epoxy-coated rebar has been in frequent use in the United States since the mid-1970s. There the main application is in the decks of highway bridges subject to de-icing salts, but all over the world the product has also been used as reinforcement in many other fields of concrete constructions, e.g. garages, substructures of marine bridges and offshore structures.

The consumption of epoxy-coated reinforcement in the USA has increased gradually from about 1,000 tons yearly in the 1970s to around 250,000 tons yearly in 1990. In Canada there are a rapidly growing number of applications. In the rest of Europe the application concentrates on single projects. The Middle East market is currently greater than 30,000 tons yearly.

4.5.2 Long time performance of coating

Corrosion performance over the long term in bridge deck applications has been reported to be satisfactory [6,8,31,32,34,38]. The results showed that epoxy-coated reinforcing steel with the possible exception of an initial experimental product, would be expected to perform significantly better than uncoated reinforcement.

A large-scale investigation concerning the applicability of epoxy-coatings to reinforcing steel bars has been conducted by the US Federal Highway Administration, with particular reference to bridges which were up to 20 years old at the time of investigation. The general result as reported in [6,31,39] is that a noticeable reduction in corrosion damage to reinforcement has taken place over the period, in which epoxy coating has been in use. The study on site and of taken specimens comprised 92 bridge decks. The results of the newest investigation [39] are as follows:

- None of the decks reinforced with epoxy-coated bars showed any visual signs of concrete deterioration which could be clearly related to reinforcement corrosion.
- The reinforcement was in 81 % free of corrosion in spite of chloride concentrations up to 3.8 mass-% in the surrounding concrete.
- In concrete cracks, the corrosion protection efficiency of the epoxy coating was clearly lower than in uncracked areas. This was related to the greater moisture content of the concrete in the cracked area and loss of adhesion of the epoxy on the steel substrate.
- Low concrete covers resulted in stronger corrosion attack.
- There was no clear relation between the corrosion protection on the one side and the number of defects in the coating and the loss of adhesion on the other.

Another extensive investigation on bridges in the USA [40] came to a very critical judgement of the behaviour of epoxy-coatings under unfavourable environmental conditions. They found, in some bridge decks and piles under maritime conditions, a massive loss of adhesion on the steel substrate in wet concrete. Therefore the investigations were extended on 18 bridge decks 3 to 20 years old [41]. Despite the fact that the product standard had been fully complied with a significant debonding around existing or introduced coating imperfections was detected in many cases. This fact was independent of the presence of chlorides in the vicinity of the reinforcement. No correlation existed between the tendency to loss steel/coating-bond and age of the structure.

One failure in performance of epoxy-coated bars has been the focus of much attention [35,42-44]. Five bridges built in the late 1970s and early 1980s, linking the Florida keys, showed severe corrosion of the substructure primary in the splash zone and evaporation zone in less than ten years. High temperatures and humidity, as well as extremely high chloride content of the surrounding seawater, created one of the harshest environments encountered in reinforced concrete applications.

With respect to the epoxy-coated bars used in these bridges, factors which promoted severe deterioration were:

- Bad workmanship of coated bars, along with poor quality of the original coating. Substrate preparation, in particular, had been inadequate (e.g. chloride contaminations on the substrate beyond the coating from the beginning). Testing showed serious coating fracture and debonding when subjected to either a standard bend test or fabrication bending.
- Corrosion was initiated in fabricated bars at bends and then progressed to straight parts.
- Cover to the bars was less than 25 mm, and in all cases below specification.

The damage included extensive metal loss, with additional localised pitting and spalling of the concrete cover. The deterioration could not be traced to any particular deviation from construction design or materials specification. The corrosion appeared to develop at imperfections in the coating, especially where debonding had taken place. Fig. 4.5 describes the sequences of damage. The corrosion may be viewed as resulting from the presence of normal production imperfections (B) which were then aggravated by fabrication and handling (C). Exposure to construction site environment, and salt water for a long time, caused significant debonding around existing or introduced coating imperfections (D). This debonding could develop in the absence of chloride ions. Experience showed debonding could also take place in chloride-free concrete (see below). Exposure to chloride containing concrete, aggravated coating delamination (D). Corrosion began at the exposed metal at imperfections and in the crevices which exist below debonded coating. A loss of epoxy's insulative properties and macrocell action (chapter 4.4.3) with cathodic regions in areas of good oxygen availability aggravated the damage.

Further, in [35] investigated structures outside the Florida Keys were found to be generally corrosion-free, but extensive metal-coating disbondment was observed whether or not significant chloride contamination existed at the rebars. It is expected that the corrosion-free service life in those structures will primarily result from good concrete quality and thick cover and not necessarily due to the use of epoxy-coated rebar.

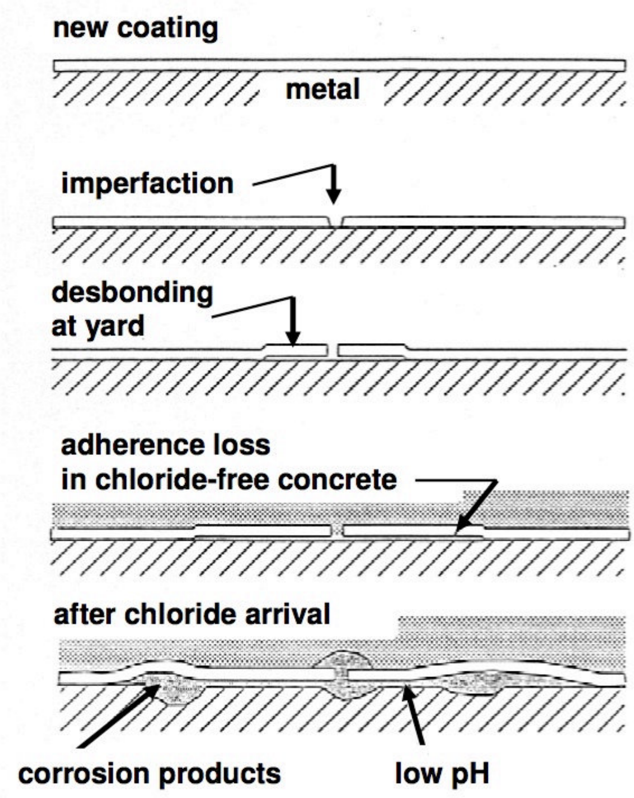

Fig. 4.5: Stages in the development of corrosion of epoxy-coated rebar in concrete [35]

4.6 Benefits from the use of epoxy-coated reinforcement

The extensive experience concerning epoxy-coated reinforcement suggests that epoxy-resin coatings are able to provide long-term corrosion protection. However, a whole range of conditions must be adequately met to maximize the performance gains in relation to uncoated reinforcement. These chiefly include:

- proper substrate preparation, including chromating,
- adequate, uniform film thickness,

- less than 3 to 4 pores per metre in coating,
- careful handling (transport, storage, steel fixing, concrete placing) to prevent damage,
- application of suitable touch-up materials for defects,
- adequate concrete cover,
- systematic maintenance of structure.

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5 Stainless steel reinforcement [1,2]

5.1 Steel types [3,4]

The term stainless steel does not refer to a single specific material, but rather to a group of corrosion resistant highly alloyed steels which in contrast to unalloyed steels, do not show general corrosion and noticeable rust formation in normal environmental conditions (atmosphere, humidity) and in aqueous, nearly neutral to alkaline media. Basic requirement for the previously mentioned reaction is a minimum concentration of that steel on particular alloying elements and the existence of an oxidising agent (e.g. oxygen) in the surrounding medium. This causes a passivation of the surface. "Passivity" describes a condition that produces a strong inhibition of the reaction of resolving iron after forming a passive layer on the surface. Chromium, in particular, is an element that tends towards passivation. A self-forming inert chromium oxide layer on the surface of the material protects against corrosion. In the event of the protective surface layer being damaged, it is self-healing in the presence of oxygen. This property is transmitted to steel through alloying. General corrosion decreases in corrosion-promoting media contrary 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 mass-%. Corrosion resistance may be further improved by additions of further alloying elements. Chromium, molybdenum and nitrogen are important elements in relation to pitting corrosion. Nickel especially increases corrosion resistance in acid media.

Changing the balance of the alloying elements (chromium, nickel, molybdenum, nitrogen, titanium and others) will influence the structure as well as the other properties other than corrosion behaviour, mechanical and physical properties and weldability. Therefore members of the stainless steel family are usually placed into groups having the same metallographic structure. Within the area of concrete reinforcement, three types of stainless steels are generally available in the required product form. These are ferritic, austenitic and ferritic-austenitic (duplex). 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, but particular technological characteristics are aimed at with regard to processing and application, as well. However, by increasing the alloy content, the cost of the material will also increase. It is therefore important to select steel types with an alloy content which is sufficiently corrosion resistant for the job to be done and having sufficient mechanical properties and weldability as well.

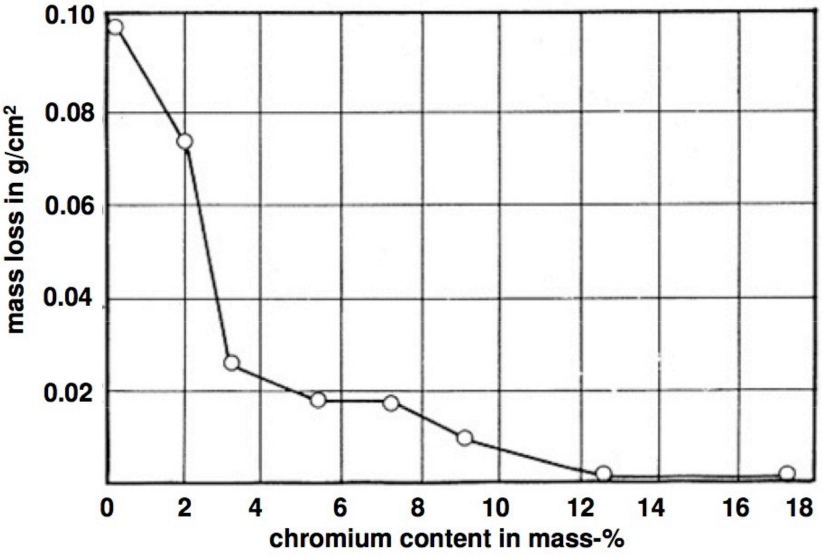


Fig. 5.1: Corrosion of chromium steels in industrial air (Binder and Brown in [3])

In common conditions, i.e. those which prevail in construction engineering (attack of light acid to alkaline aqueous media), **ferritic steels** with about 11 to 30 mass-% of chromium have a sufficient resistance against general corrosion. With an addition of a sufficient content of chromium and molybdenum up to about 2 mass-%, resistance against pitting corrosion can be achieved as well. Besides, ferrites have a high resistivity to stress corrosion cracking in a chloride-containing environment. Above all, if you assume comparable contents of chromium, the reaction of ferritic steels towards crevice corrosion is much more adverse than it is e.g. with austenitic steels.

Ferritic steels are ferromagnetic. An advantage of these steels in comparison with austenic steels is the higher yield stress in the as-rolled condition. Adversely they do possess a lower fracture-elongation, are more difficult to work and suffer brittleness at low temperatures. Their tendency towards work hardening during cold forming is low in comparison with austenitic steels. They are not so readil y weldable as the other types.

The ferromagnetic **martensitic steels** have a chemical analysis comparable to ferritic steels, but have a higher carbon content and are distinguished from all other stainless steels by a substantially higher hardness strength and lower ductility. Because of that, particularly the more common carbon martensitic steels are very sensitive to hydrogen-assisted stress corrosion cracking. However, through a limitation of the content of carbon to max. of 0.05 mass-% and the addition of up to 5% of nickel, the reaction towards stress corrosion cracking of these ”soft martensitic steels“ can be improved. Assuming a comparable content of chromium and molybdenum, and an equal surface quality, these materials can be classified similar to ferritic steels in regard of corrosion. Due to the peculiar technological properties and the unfavourable welding behaviour (tendency to hardness cracks) martensitic steels are not suitable for making reinforcing steels.

Austenitic steels have between 17 to 25 mass-% of chromium and 8 to 26 mass-% of nickel. These steels are especially used because of their positive corrosion properties and their superior workability in comparison with other stainless steels. They have a high resistance to general corrosion, pitting corrosion and crevice corrosion, but are sensitive to stress corrosion cracking in their typical chemical analysis with about 10 mass-% nickel. The resistance to pitting corrosion, crevice corrosion and stress corrosion cracking can be improved with an addition of chromium, molybdenum and nickel.

Austenitic steels are not ferromagnetic. They have a higher toughness and a much better weldability but a lower yield-strength in the as-rolled condition than ferritic steels. The tendency to work-hardening is very pronounced. For that reason austenitic stainless steels can increase their strength significantly by means of cold forming without unacceptable reduction of deformability. The ductility of austenitic stainless steel always exceeds that of conventional bars, and they have a very high toughness as well as possessing good ductility properties at low temperatures. In seismic areas, austenitic steels are often used in reinforced concrete structures, as their strength and ductility intensify the materials specific deformation energy. This is advantageous for absorbing the impact of a violent earthquake.

Ferritic-austenitic (duplex) steels have a binary structure of ferrite and austenite. The typical range of their chemical analysis is 22 to 28 mass-% of chromium, 4 to 8 mass-% of nickel. Molybdenum can be added in order to improve the corrosion resistance. These steels combine good properties of ferritic steels (high yield strength) and austenitic steels (good ductility, improved corrosion properties). Owing to their excellent mechanical properties (high yield strength, good ductility) in the as-rolled condition, and the very high resistivity to chloride attack, duplex steels are of interest as material for reinforcement.

Table 5.1 lists the chemical composition of the main stainless steels suitable for the manufacturing of reinforcing stainless steels. This survey was taken from a common European standard [5] which in 2008 was in preparation (see section 5.5). It was supplemented by the ferritic steel type 1.4003, which is used in Germany and other countries. The numbers of the steels are according to European Standard codes as given in EN 10088 [6].

5.2 Types of corrosion of stainless steel

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 to general corrosion, but are sensitive to local corrosion in the presence of specific media (e.g. chloride ions), particularly when they contain insufficient alloy content. There are four types of corrosion of stainless steels to be observed: general corrosion, intergranular corrosion, pitting corrosion and stress corrosion cracking. The performance of the different stainless steels is now considered in relation to these corrosion types.

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 steels must have higher contents of particular alloying elements in order to reduce corrosion wastage or to achieve passivity. It is important, that the corrosion rate in the active state decreases very much, if there is an increasing pH value. Corrosion resistance generally exists above pH 4 and therefore, in weakly acidulous media, as well in a usual atmosphere. Chromium steels, with > 12 mass-% of chromium, as well as all more highly alloyed steels are passive in an alkaline media. A passivated steel cannot therefore corrode in a medium such as concrete. The passive film is also stable if the concrete is carbonated [7].

Table 5.1a: Ferritic steel - chemical composition according to [6]

steel designation		mass-%											grades
steel name	steel No.	C	Si	Mn	P	S	N	Cr	Mo	Ni	Ti	others	
X3CrNb 17	1.4511	≤ 0.05	≤ 1.00	≤ 1.00	≤ 0.040	≤ 0.015	-	16.0 to 18.0	-	-	-	Nb: 12xC to 1.00	InE235
X2CrNi 12	1.4003	≤ 0.03	≤ 1.00	0.50 to 1.50	≤ 0.040	≤ 0.015	≤ 0.03	10.5 to 12.5	-	0.30 to 1.00	-	C+N≈ 0.03	InE500

Table 5.1b: Austenitic steels - chemical composition according to [6]

steel designation		mass-%											grades
steel name	steel No.	C	Si	Mn	P	S	N	Cr	Cu	Mo	Ni	others	
X5CrNi 18-10	1.4301	≤ 0.07	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.030	≤ 0.11	17.0 to 19.5	-	-	8.0 to 10.5	-	InE235, InE500, InE650
X2CrNiN 18-10	1.4311	≤ 0.030	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.030	0.12 to 0.22	17.0 to 19.5	-	-	8.0 to 11.5	-	InE235, InE500, InE650
X5CrNiMo 17-12-2	1.4401	≤ 0.07	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.030	≤ 0.11	16.5 to 18.5	-	2.0 to 2.5	10.0 to 13.0	-	InE235, InE500, InE650
X2CrNiMoN 17-13-3	1.4429	≤ 0.030	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.015	0.12 to 0.22	16.5 to 18.5	-	2.5 to 3.0	11.0 to 14.0 [b]	-	InE235, InE500, InE650
3CrNiMo 17-13-3	1.4436	≤0.05	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.030	≤ 0.11	16.5 to 18.5	-	2.5 to 3.0	10.5 to 13.0 [b]	-	InE235, InE500, InE650
X6CrNiMoTi 17-12-2	1.4571	≤0.08	≤ 1.00	≤ 2.0	≤ 0.045	≤ 0.030	-	16.5 to 18.5	-	2.0 to 2.5	10.5 to 13.5 [b]	Ti:5xC to 0.70	InE235, InE500
X1NiCrMoCu 25-20-5	1.4539	≤ 0.020	≤ 0.70	≤ 2.0	≤ 0.030	≤ 0.010	≤ 0.15	19.0 to 21.0	1.2 to2.0	4.0 to 5.0	24.0 to 26.0	-	InE235, InE500, InE650
X8CrMnCuNB 17-8-3 [a]	1.4597	≤ 0.10	≤ 2.00	6.5 to 8.5	≤ 0.040	≤ 0.030	0.015 to 0.30	16.0 to 18.0	2.0 to3.5	≤ 1.00	≤ 2.0	B: 0.0005 to 0.0015	

[a] Stainless steel whose manufacturing process is patented, mentioned in prEN 10088-3:2002.

[b] When for special reasons, e.g. low magnetic permeability, it is necessary to minimize the ferrite delta content, the maximum Ni content may be increased of the following values: 0.50 % (m/m) : 1.4571; 1.00 % (m/m) : 1.4429, 1.4436

Table 5.1c: Ferritic-austenitic (duplex) steels - chemical composition according to [6]

steel designation		mass-%											grades
steel name	steel No.	C	Si	Mn	P	S	N	Cr	Cu	Mo	Ni	others	
X2CrNiMoN2 22-5-3	1.4462	≤ 0.030	≤ 1.00	≤ 2.00	≤ 0.035	≤ 0.015	0.10 to 0.22	21.0 to 23.0	-	2.50 to 3.50	4.50 to 6.50	-	InE500, InE650, InE800

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

Stress corrosion cracking can occur when an appropriate combination of factors such as material, specific environment and stress level are present. As the tendency to stress corrosion normally increases with increasing chloride content and 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. Stress corrosion cracking is 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 of the research described in ref. [1] (section 5.8.1).

The resistance of stainless steels to chloride-assisted stress corrosion cracking decreases in the following order: ferritic chromium steels, ferritic-austenitic steels, austenitic chromium-nickel (molybdenum) steels. This can above all be explained by the influence of the nickel content on the sensitivity to stress corrosion cracking of steels containing a high portion of chromium. A minimum resistance exists at about 10 mass-% of nickel. From this minimum, resistance decreases, depending on rising or reducing content of nickel. In martensitic stainless steels, the reaction towards hydrogen-assisted stress corrosion cracking is decisive [8].

The corrosion resistance required for use in concrete is primarily a resistance against localized corrosion **(pitting, crevice corrosion**) in chloride containing media [1]. In the case of pitting corrosion, an interaction between chloride ions and the passive layer develops, in which 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. It occurs whenever structural elements are in more or less narrow contact with each other and crevices develop. On this occasion, we can get a concentration of chloride ions underneath corrosion products in the crevice, and therefore a decline 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 conditions than does pitting corrosion in areas which are free of crevices.

The danger of pitting corrosion and crevice corrosion decreases with a decline of chloride content, declining temperature and rising pH value. 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. 5.10 (section 5.8.1). 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 [9]. However, stainless steels are basically more resistant in concrete construction with a pH value of about 8 to 13 than e.g. in atmospheric weather conditions. As a result, the standard requirements for reinforcing steels and e.g. anchorage devices in concrete are normally more modest than for structural elements in open atmospheres.

Corrosion resistivity in a media that generates local corrosion, further depends on the steel composition as well as its surface condition. Improvement in resistance to pitting corrosion and crevice corrosion takes the following order: scaled, raw grinded, blasted, fine ground, pickled, polished.

Weld joints are above all more exposed to the danger of pitting corrosion than are similar non-welded steels, since oxide films (temper colours) or scale layers will have developed in the weld joint area during welding, because of incomplete or lacking 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 [10] and it can destroy the low cathodic activity of stainless steel [11]. In a lot of cases this problem can be solved by pickling or shot blasting the weld. Pickling is however, not a practical solution in industrial fabrication involving on-site welding of stainless steel.

Pitting and crevice corrosion are especially influenced by the alloying elements of chromium, nickel, molybdenum and also nitrogen. In order to compare stainless steel grades with different alloy contents, a correlation of the influence of the different elements has been made, resulting in the expression of pitting resistance equivalent (PRE). This expression can be considered as a relative measure of the total resistance resources for the steel grade and thus a comparable value. The expression is calculated from the content of the following alloying elements in the steel grade:

PREN = 1.0 x % chromium + 3.3 x % molybdenum + 16 x % nitrogen

Nickel improves the corrosion resistance under conditions of crevice corrosion, as it raises the resistivitiy to acid.

The susceptibility to pitting and crevice corrosion decreases in the order Cr-Ni-Mo steel, Cr-Ni steel, Cr steel. Examples of commercially available standard grades, which can be used in concrete, and their equivalent pitting resistance are shown in Table 5.2. The materials are arranged with increasing corrosion resistance in descending order in the table and also with increasing cost of the materials. In general most of the stainless steels used for reinforcement are within the types 1.4301 and 1.4401/1.4571 and 1.4462. Only in extreme environments more resistant materials considered.

Table 5.2: Composition of stainless steels available in a product form for use as reinforcement [6]

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	X1NiCrMoCu 25-20-5	austenitic	38
1.4529	X1NiCrMoCuN 25-20-7	austenitic	42

5.3 Production of stainless steel reinforcement [1,4,12]

For application in concrete structures, ferritic, austenitic and ferritic-austenitic (duplex) steels can be produced as ribbed bars within the normal range of strength and deformability requirements. Up to 14 mm diameter, the bars are available in rings permitting the fabrication of any shape and length of reinforcing bar. Above 14 mm diameter the bars are supplied in straight lengths (length up to 12 m are available in the UK).

One of the initial problems in producing stainless steel reinforcing bars was that the yield strength ($Rp_{0.2}$) of ferritic, and more importantly austenitic as-rolled bars were approximately the same as those of mild steel. The general mechanical properties in the annealed condition are such that the yield strength of ferritic and austenitic types are about 300 N/mm^2 and 200 N/mm^2 respectively, whereas the corresponding values for duplex steels are higher (400 - 480 N/mm^2). Therefore no ferritic or austenitic steel in the normal as-rolled condition would have sufficient strength.

However, in order to meet the requirement for use as reinforcement in concrete the strength of the steels must be increased. As these steels had a metallurgical structure incapable of being hardened significantly by heat treatment, other methods of increasing strength had to be pursued.

Subsequent treatment, either by special heat treatment or cold and warm working, including an increase in the nitrogen content, will enable high yield reinforcement strength to be achieved. These processes are however complicated and increase the high material cost of stainless steel.

Ferritic steels in the as-rolled condition have a higher yield strength than austenitic steels. There is a probability that the bars may be further strengthened by cold twisting [13] or drawing and cold rolling [7]. These processes can be facilitated by employing a special alloy composition. In this case, the carbon and nitrogen contents are limited to avoid hardening after cooling from the austenite phase. The steel retains sufficient strength and deformation properties after cold deforming from 4 to 14 mm diameter. In addition to strengthening the bars, twisting is also an effective method of removing millscale, which has been found to aggravate pitting corrosion and was previously removed by pickling and shot blasting.

Acceptable high yield reinforcing bar strengths can be obtained from **austenitic stainless** steels. The smaller sizes, from 4 to 14 mm, may be strengthened by means of cold working (drawing and rolling) [7,12,14]. For the austenitic types, cold working results in a reduction of the elongation from 40 % to 20 - 25 %, which is sufficient for the rebars in concrete.

The literature [15] sometimes makes reference to the possibility of a somewhat reduced corrosion resistance of cold worked austenitic stainless steel, whereas in duplex materials this is not the case. Cold working of austenitic stainless steel may cause a transformation of some of the austenite into martensite. Alloys with a lower content of alloying elements (e.g. 1.4301) are more prone to develop martensite than those alloys with a higher content (e.g. 1.4539) (see section 5.4.2). A martensitic structure favours pitting corrosion. However, the amount of cold work of reinforcing steel does not usually exceed about 35 %, which results in not damaging martensite formation and therefore a reduction in the resistance to pitting corrosion [7]. For small dimensions (< 12 mm), also warm working at reduced temperature may be used for increasing the strength of austenitic steels resulting in mechanical properties similar to those obtained by cold working [12,14]. An effective solution for large diameter bars, up to

40 mm for ribbed bars and 50 mm for plain bars, is the combination of using a modified composition (an addition of 0.15/0.20 mass-% 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 [7] such wires are cold deformed, in Italy [16] they are as-rolled or cold deformed.

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 reinforcing bar [17]. In this approach, a core of ordinary steel is encapsulated in a stainless steel sheath to resist corrosion. However, the difficulties associated with inserting the core and fusing the metals together added to the cost, which thereby offset the savings resulting from the use of a cheaper core. Furthermore, if pinholes were present in the cladding there was a potential problem of 'undercutting' corrosion [14]. At present improved products are on the market in the UK.

5.4 Structural properties

Mechanical and physical properties, as well as welding behaviour, are very important in order to evaluate the ability of any material to withstand the expected loads during the designed service life. These depend on the method of manufacture, material composition, microstructure and bar size.

5.4.1 Mechanical properties

The mechanical properties of stainless steels that are of main concern to the designer are characteristic strength, ultimate tensile strength and elongation. The stress-strain behaviour of austenitic and duplex grades differs from that of carbon steels, in that they do not exhibit a well-defined yield point when test pieces are submitted to tensile load. To characterise the design strength of such materials, proof strengths are used and are determined as the stress $Rp_{0.2}$ belonging to 0.2 % residual strain after unloading. After [18], a modulus of elasticity for austenitic and ferritic-austenitic stainless steel reinforcement of 200 kN/mm^2 may be used in design, except for the austenitic steel 1.4529, which has a modulus of 195 kN/mm^2. The tables 5.3 – 5.5 show typical properties for different steel grades from the UK, Germany and Italy.

Table 5.3: Mechanical properties of stainless reinforcing steels in the UK (from [12] and steel maker information)

steel grade	**chemical composition**	**condition**	**bar size** [mm]	**yield strength** [N/mm^2]	**tensile strength** [N/mm^2]	**elon-gation** [%]
1.4401 austenitic	X5CrNiMo 17-12-2	warm worked 1)	10	865	1000	20
			20	745	880	25
			32	620	775	25
			40	550	685	25
		as rolled 2)	25	279	579	52
		cold twisted 2)	20	660	780	28

1)minimum values 2)values of specific specimens

Temperature influence

Austenitic stainless steels in the warm deformed condition retain considerably higher strength than carbon steels, ferritic and ferritic-austenitic (duplex) stainless steels at **elevated temperatures** [18,19]. At temperatures up to 500 °C, there is negligible reduction in the 0.2 % proof stress. This suggests that concrete elements reinforced with austenitic stainless steel will behave better in fire than conventionally reinforced elements with the same depth of cover.

Table 5.4: Mechanical properties of stainless reinforcing steels in Germany (from [6] and steel maker information)

steel grade	**chemical composition**	**condition**	**bar size** [mm]	**yield strength** [N/mm^2]	**tensile strength** [N/mm^2]	**elon-gation** [%]
1.4429 austenitic	X2CrNiMoN 17-13-3	hot 4) rolled	10	880	990	20
			20	790	900	25
			32	630	790	25
			40	550	790	30
1.4571 austenitic	X6CrMiMoTi 17-12-2	cold 3) rolled	10 1)	456	599	39
1.4462 ferr.-aust.	X2CrNiMoN 22-5-3		7 1)	870	934	13
1.4003 ferritic	X2CrNi 12		8 1)	518	608	16
		hot 2) rolled		~350	~490	~25

1) 6-14 mm is possible 2) no reinforcing steel
3) values of specific specimens 4) minimum values

Table 5.5: Mechanical properties of stainless steels in Italy (from [16] and steel maker information)

steel grade	**chemical composition**	**condition**	**bar size** [mm]	**yield strength 1)** [N/mm^2]	**tensile strength 1)** [N/mm^2]	**elon-gation 1)** [%]
1.4301	X5CrNi 18-10	cold finished	10	671	831	21.4
1.4307	X2CrNi 18-9	hot rolled	20	761	864	27.9
1.4401	X5CrNiMo 17-12-2		32	754	863	25.9
1.4404	X2CrNiMo 17-12-2		40	717	878	31.1
1.4571	X6CrNiMoTi 17-12-2					
1.4462	X2CrNiMoN 22-5	cold finished	10	950	1059	14.0
1.4362	X2CrNiN 23-4	as rolled	18	485	668	-

1) values of specific specimens

The increase in strength of stainless steels produced using a cold working process gradually reduces with increasing temperature. At 500 °C, austenitic stainless steels exhibit a marginal decrease in the 0.2 % proof strength and a significant reduction in the ultimate tensile strength. The strength of heated, cold deformed stainless steel reaches the strength of annealed material at a little over 800 °C.

For example, liquefied natural gas is stored at a **low temperature** of -165 °C and liquid oxygen below -190 °C. Any materials forming part of a containment system for such gases must have satisfactory and predictable properties at these temperature to avoid failure. Austenitic stainless steel reinforcement, which retains ductility to temperatures as low as -196 °C, is suitable for use in such applications [18,19], unlike carbon steel, which exhibits a transition from ductile to brittle behaviour well above this temperature. The ultimate tensile strength and the 0.2 % proof stress increase slightly with descending temperature. The elongation decreases. The changes are similar for cold worked austenitic steels. Ferritic-austenitic (duplex) and above all ferritic stainless steels undergo a marked decrease in toughness at sub-zero temperatures. These steels are not recommended for cryogenic applications.

Fatigue

Fatigue failure of a metal is defined as failure under repeated application of a cycle of stress. Stainless steel bar has fatigue properties equal to that of carbon steel when tested in air [18]. Corrosion fatigue is the failure of metals under repeated cycles of stress while exposed to corrosive attack. Corrosion fatigue is influenced by the same factors as fatigue, and also by frequency (time) and by the corrosive effect of the environment. Because of its excellent corrosion resistance, stainless steel has enhanced corrosion fatigue properties [4].

5.4.2 Physical properties

The important physical properties of stainless steel considered in relation to application in concrete are: density, thermal conductivity, coefficient of thermal expansion and magnetic permeability. In Table 5.6, typical values of these parameters for different types of stainless steel in the annealed condition are collected.

From the structural point of view, the most important physical property is the coefficient of linear thermal expansion [1]. The coefficients of thermal expansion of ferritic steel and concrete are more or less the same (12 and 11 x 10^{-6} K^{-1} respectively). In comparison, the coefficient of thermal expansion of austenitic stainless steel is higher (17 x 10^{-6} K^{-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 coefficient of steel and concrete. This may in theory cause some minor defects in the contact zone, as well as expansion cracking, particularly in heavily reinforced sections. However, there are no practical evidence or laboratory results supporting this assumption. Compared to carbon steels, the higher coefficients of thermal expansion for the austenitic steels, and the lower thermal conductivities, may give rise to greater welding distortions (section 5.4.3).

Table 5.6: Physical properties of stainless steel

	density [g/cm^3]	**thermal conductivity** [W/m · °C]	**specific heat** [J/g · °C]	**coefficient of thermal expansion** [K^{-1}]	**magnetic**
ferritic steel	7.7	23	0.46	12x10^{-6}	yes
austenitic steel	7.8-8.0	12-15	0.44	17x10^{-6}	no
martensitic steel	7.7	23	0.46	12x10^{-6}	yes
duplex steel	7.7	20	0.44	13x10^{-6}	yes

Ferritic and martensitic stainless steels are (ferro-)magnetic, as are carbon steels. The magnetic behaviour of the various types of austenitic steels vary, but they have low magnetic permeabilities compared to other ferrous steels and are generally considered to be non-magnetic.

Relative magnetic permeability is defined as the ratio of the magnetic flux density produced in the material, to that produced in free space by the same magnetising force; thus the lowest achievable magnetic permeability is 1. For austenitic stainless steels, magnetic permeability depends on chemical composition and production process. Concerning the steel grade, magnetic permeability decreases in the designation order 1.4301 - 1.4401 - 1.4436 - 1.4429 - 1.4529. However, the values vary with production process, e.g. values for cold-drawn steel bar are greater than for bar that has been warm-worked. Heavy cold working, particularly of the lean alloyed austenitic steel, can also increase magnetic permeability; subsequent annealing would restore the non-magnetic properties. Cold working produces phase transformation from austenite to martensite (section 5.3). These strain induced martensite phases are magnetic and increase magnetic permeability. In particular the grades more highly alloyed with chromium, manganese, nickel, molybdenum and nitrogen alloyed grades have an increased austenite stability and are effectively non-magnetic after cold deformation (lit. in [8]). Therefore bars required to have a low permeability (~ 1.005) must be hot-rolled and/or be of a specific composition.

5.4.3 Weldability

All stainless steel can be welded, either to themselves or to carbon steel, provided that necessary precautions are taken [18,19]. However, welding method and type of weld should be considered. Welding of reinforcement can be made by resistance welding as well as metal arc welding. As most materials used for reinforcement have been strengthened by cold working, reduction of strength at the weld is possible depending of the heat input applied.

Resistance welding is the most widely used welding method in factories. It is used for prefabrication of mesh reinforcement. Resistance welding, having generally the lowest heat input will have the least effect on the properties. On the other hand, it requires well adjusted parameters in order to obtain a mechanical connection that is able to transfer sufficient force. This is done by optimising the electrical parameters along with the press force by welding.

Gas metal arc welding (MIG/MAG) is the most frequently used method for welding carried out on site. It is a very rational method for joining crossing rebars. When arc welding reinforcing bars, some loss of tensile and yield strength may result from the welding heat.

Consequently it is advisable to adjust the welding parameters resulting in shortest possible welding time and the best possible gas shielding. The latter is in order to minimise oxide formation. Gas mixture used is 96 % argon, 3 % CO_2 and 1 % hydrogen. If the weld products (temper colours) followed by high heat input metal arc welding are not completely removed, corrosion resistance is reduced. Pickling or shot-blasting the weld can often solve this problem, but is not always possible on construction sites.

The weldability of stainless steel depends on its structure and chemical composition. The weldability of the steel types is best for the austenitic types, similar but more restricted for the duplex materials, and very limited for the ferritic ones. Weldability is improved by decreasing the carbon content, increasing the nickel content and by stabilisation. As a rule, low carbon grades of stainless steel with max. C = 0.03 % or with titanium or niobum stabilised grades can be welded without fear of any detrimental effect.

In comparison with carbon steel, the higher thermal expansion of austenitic stainless steel, coupled with its lower value of thermal conductivity, increases the possibility of distortion occurring during the welding process. However, the higher electrical resistance of stainless steel is an advantage because it results in the generation of more heat for the same current. Together, with the low heat conductivity, this can be advantageous when resistance welding processes are used.

When welding the duplex stainless steels, it is the cooling rate which controls the micro-structure, therefore the heat input should be controlled in conjunction with the material thickness to obtain the correct weld structure.

Because stainless steel concrete reinforcing bars have different chemical compositions it is important to select welding electrodes or wires which result in welds with identical or better composition to those of the bars and that provide weld filler with corrosion resistance properties as nearly identical to the base metal. Proper weld rod selection not only preserves corrosion resistance properties, but is also important in achieving optimum mechanical properties.

When welding stainless steel to carbon steel, the electrode or wire has to be of a higher alloy content than the stainless steel that is to be welded in order to compensate for the diluting effect of the carbon steel. The chemical composition of weld, depending only on the welding electrode or wire used, shall not be too lean in alloying elements, otherwise brittle welds will result. As a minimum the weld should have the composition of stainless steel type 1.4301. This can be achieved with an electrode or wire that contains at least 23 % chromium and 12 % nickel.

5.5 Current specifications

UK

BS 6744 [20] was one of the first standards covering stainless steel reinforcement. This standard specifies stainless hot-rolled and cold-worked steel bars to achieve characteristic strength levels of 500 N/mm^2 or higher. Strength grades are defined in Table 5.7. Grade 200 steel is only available as plain bar.

Table 5.7: Minimum tensile properties

strength grade	**0.2 % proof-strength $R_{p0.2}$** [N/mm^2]	**stress ratio $R_m/R_{p0.2}$**	**elongation at fracture A_3** [%]	**total elongation at maximum force A_m** [%]	**nominal size** [mm]
200	200	1.10	22	5	3-50
500*	500	1.10	14	5	6-50
650	650	1.10	14	5	3-25

*recommended grade

In the UK, stainless steel is currently produced from the austenitic and ferritic-austenitic materials 1.4301, 1.4436, 1.4429, 1.4462, 1.4501, 1.4529. They are listed from left to right in order of increasing corrosion resistance and, consequently, of increasing initial cost. In most situations, standard austenitic grades 1.4301 or 1.4436 will provide an acceptable solution when designing against corrosion. The higher grade austenitic and ferritic-austenitic steels should be considered when the possibility of high levels of chloride build-up in concrete over time is anticipated (e.g. marine structures or traffic structures heavy contaminated with de-icing salts). These materials are typically available in all three strength grades; however the duplex steel designation 1.4462 is only available in 650 grade.

The range of sizes of bars shall be from 3 mm to 50 mm. Typical mechanical properties are listed in Table 5.3.

Germany

In Germany there exists an approval of the Deutsches Institut für Bautechnik in Berlin concerning stainless reinforcing steels [21]. The application of these steels has up to now been limited because of the high price.

Small diameters of 4 to 14 mm are cold rolled plain or ribbed bars and are of the ferritic type 1.4003, the austenitic type 1.4571 and the ferritic-austenitic (duplex) type 1.4462. The wires are weldable and also used for welded wire mesh. Typical mechanical properties are documented in Table 5.4. The strength grade corresponds to the British Standard strength grade 500, but the elongation at fracture is 10 %. It is recommended to use the grades 1.4571 and 1.4462 if the possibility of high levels of chlorides is to be expected. The steel grade 1.4003 may be used if quick carbonation of concrete cover can not be excluded reliably.

Further, in Germany, bars of 10 to 40 mm are offered in the hot rolled condition. With the austenitic steel grade of 1.4429, a yield stress of 550 to 880 N/mm^2 can be reached (Table 5.4).

USA

In the USA, stainless steel reinforcement is specified in ASTM A955M-2001 [17], which covers deformed bar in a wide range of alloys and plain stainless steel clad carbon steel bars from 9.5 to 57.3 mm diameter. In particular, austenitic stainless steels with designation numbers 1.4429 and 1.4404 are often used, and typical ferritic-austenitic (duplex) stainless steels are types equivalent to 1.4462. They are generally of one of three minimum yield levels, 300, 420 and 520 N/mm^2, designated as grade 300, 420 and 520, respectively.

Other countries

In Denmark, cold rolled weldable austenitic stainless steel in smooth and profiled bars of the types 1.4301 and 1.4401 are in use [10]; dimensions from 4 - 16 mm are available. Resistance welding is the most widely used welding method. It is for instance, used for prefabrication of mesh reinforcement. MIG/MAG welding is the most frequently used method for welding carried out on site. Also, in other Scandinavian countries, steel types 1.4301 and 1.4401 are specified. In Norway and Finland the steel type 1.4436 has been used.

In Italy, mainly austenitic stainless steels 1.4301 and 1.4401 and ferritic-austenitic (duplex) steels of grade 1.4462 and 1.4362 have been used in reinforced concrete structures (Table 5.5).

In France, the low austenitic carbon steel types 1.4307 and 1.4404 are specified.

Many specifications in the Middle East are based on BS 6744 [20], particularly using 1.4401 steel. Duplex steel 1.4462 has been used in repair contracts in the Middle East. In parts of the Far East, such as China, Japan and India, the American codes are generally used.

European standard

At present a European standard [5] is in preparation. This standard specifies the requirements for the chemical composition, mass per unit length, dimensional, mechanical, technological and shape properties of bars and coils (wire rod and wire) of reinforcing stainless steel, smooth of grade InE235 and smooth, ribbed or indented of grades InE500, InE650 and InE800, with nominal diameters between 5 mm and 50 mm. The designation of reinforcing stainless steels covered by this standard consists of the indication of the specified proof strength of the product.

The tensile mechanical properties shall be in accordance with the requirements of Table 5.8. The specified values are a 0.05 fractile for $R_{p0.2}$ and 0.10 fractiles for the ratio $R_m/R_{p0.2}$ and A_{gt}, to which minimum values are associated.

The Table 5.1a-c lists the chemical composition of the main stainless steels, suitable for the manufacturing of reinforcing stainless steels. For each of these steels, the grades that are possible are indicated in the last column of the tables; achieving these grades depends on the diameter of the product, its manufacturing process (hot or cold rolling) and its profile (smooth, indented or ribbed). The steels mentioned may be welded under certain conditions.

Table 5.8: Mechanical properties in [5]

steel grade	**0.2 % proof-strength $R_{p0.2}$** N/mm^2		**ratio $R_m/R_{p0.2}$**		**total elongation at maximum force A_m** %	
	fractile value	minimum value	fractile value	minimum value	fractile value	minimum value
InE235	235	220	1.15	1.12	8	7
InE500	500	475	1.10	1.08	5	4
InE650	650	625	1.10	1.08	5	4
InE800	800	775	1.10	1.08	5	4

For the proposed steels in Table 5.1 (excepting the steel 1.4003), the standard gives guidelines for the selection of stainless steels depending on the conditions of use and environment, as well as example of application. However, this recommendation for use is not quite straight forward, is too complicated and seems not to be covered by research and practical experience.

5.6 Considerations of handling and design [18,19]

In order that the full corrosion resistance of stainless steel is preserved, the surface of the bars should be clean at the time of installation and must be free from mill scale. It is normal practice for hot-rolled and warm-deformed stainless steels respectively, to be delivered in a descaled condition. The presence of scale or oxides on stainless steel reinforcement should also be avoided, because it can increase the risk of galvanic corrosion. Foreign rust on the surface of stainless steel can act as a cathode and may impair the corrosion properties.

Stainless steels can be bent to shape using the methods commonly used for carbon steel. However, these steels tend to have more 'spring' than carbon steel, which needs to be taken into account when bending the steel. To bend stainless steel, the bars need to be initially over-bent, to compensate for this spring back. More force is required to bend stainless steel than carbon steel reinforcement.

In most applications stainless steel reinforcement will be used in conjunction with carbon steel reinforcement and in many instances the two materials will be in contact. Research into galvanic corrosion (section 5.9) has shown that the consequences of galvanic coupling of carbon steel with stainless steel are negligible in most situations. No particular precautions are considered necessary to eliminate this risk when carbon steel is lapped with stainless steel reinforcement and bars are cast in new concrete. For repairs and strengthening to existing concrete structures, stainless steel should not be in contact with carbon steel in areas where the existing concrete has high chloride levels [22]. At these locations, the remaining carbon steel may already be active and thus vulnerable to bi-metallic corrosion with the stainless steel reinforcement.

It should be noted that in accordance with available literature [18,22], the use of corrosion resistant reinforcement allows the durability requirements developed for carbon steel to be relaxed. Due to the high corrosion resistance of stainless steel reinforcement, consideration may be given to reducing the cover to the steel, providing that the quality of the cover concrete is maintained. Such reduction can only be considered if the reduced depth of cover allows proper placement of the concrete and a correct concrete specification is given. However, if stainless steel reinforcement is used in a highly corrosive environment, it is recommended that the minimum cover should still be at least 40 mm. The option to reduce cover depth if using stainless steel reinforcement instead of black steel is not recommended by e.g. German designers.

5.7 Practical experiences with application

Stainless steel reinforcement has been used in concrete structures in the UK, USA, Italy, France, Denmark, Norway, Sweden, Finland, Germany, in the Middle and Far East, and South Africa. Typical applications of stainless steel reinforcement are structures which are exposed to very aggressive environments.

Only relatively small quantities of stainless steel reinforcement have been used in the past. However, an increasing amount of austenitic or ferritic-austenitic (duplex) steel reinforcement is to be found in bridge engineering, multi-storey car park decks, tunnels and underpasses, retaining walls, marine structures like piers at the sea coast, where influence of seawater or de-icing salt cannot be excluded, and historic buildings and buildings with long service lives [2,18,19,22-24]. Further, these steels are generally located at construction joints or critical gaps between columns and deck.

Ferritic stainless steels are used as reinforcement in pre-cast elements of normal-weight and light-weight concrete. Another typical application is in prefabricated wall elements with inner heat insulation, where the reinforcement connects the outer and inner concrete walls [25].

The experiences are positive; core samples taken after some years and long-term monitoring of embedded corrosion probes showed no sign of corrosion of the stainless steel reinforcement [2,18]. However, no extensive long-term experiences with the use of stainless steels as reinforcement in concrete exist. In [26] a case of long-term application of stainless steel reinforcement (steel grade 1.4301) from the Mexican Gulf is reported. Due to the harsh environmental exposure of concrete piers (hot and humid marine environment) it was decided to use stainless steel in selected areas. 60 years after construction no significant corrosion was found for the reinforcement with a cover larger than approx. 20 mm, despite the extremely high chloride contents of up to 1.9 % Cl^- of dry concrete weight. For other piers at the same place reinforced with ordinary carbon steel, serious chloride and/or carbonation-induced corrosion problems occurred.

5.8 Corrosion behaviour

5.8.1 Reported corrosion resistance

A number of corrosion tests have been made with stainless steel rebars, both on a laboratory scale as well as in simulated and natural seawater environments [1]. The following tests have been conducted:

- Electrochemical tests involving metal/solution electrolyte or metal/concrete electrolyte systems. The electrochemical tests involve the application of constant current, constant potential, or measurement of the free corrosion potential of the electrode/electrolyte system. Whilst they have the advantage of providing basic information on the relevant corrosion mechanisms, however, they cannot reproduce the complex conditions encountered in service.

- Accelerated laboratory tests carried out on reinforced concrete specimens in which corrosion has been related to weight loss and pit depth measurement after fixed periods of time. The usual method adopted are embedding in concrete where chlorides were added, immersion of the specimen in chloride solution or intermittent exposure to a salt spray. The tests give a quick assessment of the relative behaviour of different steels but do not always produce the same results as long term site tests.

- Long-term site exposure tests of reinforced concrete specimens (e.g. beams which have been stressed to produce fine cracks) in realistic environments. These tests are generally thought to provide the most realistic means of assessing the true behaviour of steel in concrete. Their disadvantages are that they take a long time for results to be obtained. The appearance of rust staining, concrete cracking, weight loss and pitting have been used to monitor the progress of corrosion. The tests can also examine the effect of concrete quality, chloride concentration, depth of cover and cracks in the concrete after long term exposure to aggressive environments.

Investigation 1 [27,28]

In a ten-year study in the UK, a variety of stainless steels, such as the ferritic types 1.4002 (X6CrAl13), 1.4016 (X6Cr17) and the austenitic types 1.4301 (X5CrNi 18-10), 1.4401 (X5CrNiMo 17-12-2), were compared with unalloyed, weathering and galvanised steel using site exposure and laboratory testing. The surface of the stainless steels was 'descaled'. The steels were used as reinforcement for small prisms fabricated with various qualities of concrete cast to different thickness (Table 5.10). The concrete cover was 10 and 20 mm. A wide range of chlorides (between 0 and 3.2 mass-%) were added to the concrete and the specimens, after curing, were exposed to natural environments. The durability of the reinforcement was estimated by measurement of the development of concrete cracking, weight loss and extent of pitting.

Table 5.10: Listing of the applied concretes in investigation 1

	high	**low**
	permeability	
aggregate / cement ratio	8 : 1	6 : 1
water / cement ratio	0.75	0.60
cement content (kgm^{-3})	220	290
28d cube strength (N/mm^{-2})	29	42

The results indicated that weathering and galvanised steels are unsuitable for use as corrosion resistant reinforcement in heavily chloride-contaminated concrete. It appears that the additional corrosion resistance of ferritic stainless steels is of advantage in comparison with unalloyed steel when embedded in concretes containing low chloride levels. At high chloride levels the ferritic steels suffered severe pitting attack which was concentrated at a few points on the surface: in the poor concrete this occurred above 1 - 2 mass-% Cl^- and in the higher quality concrete above 2 - 3 mass-% Cl^-. When the concrete cover was reduced, then the corrosion intensity increased. The strongest effects occurred at isolated points, where carbonation had reached the steel surface. All the austenitic stainless steels showed very high corrosion resistance in all the environments tested. No serious corrosion was observed on any of the bars.

Figures 5.2.a – 5.2.c show the weight loss of unalloyed and high alloyed ferritic and austenitic steels with respect to chloride content.

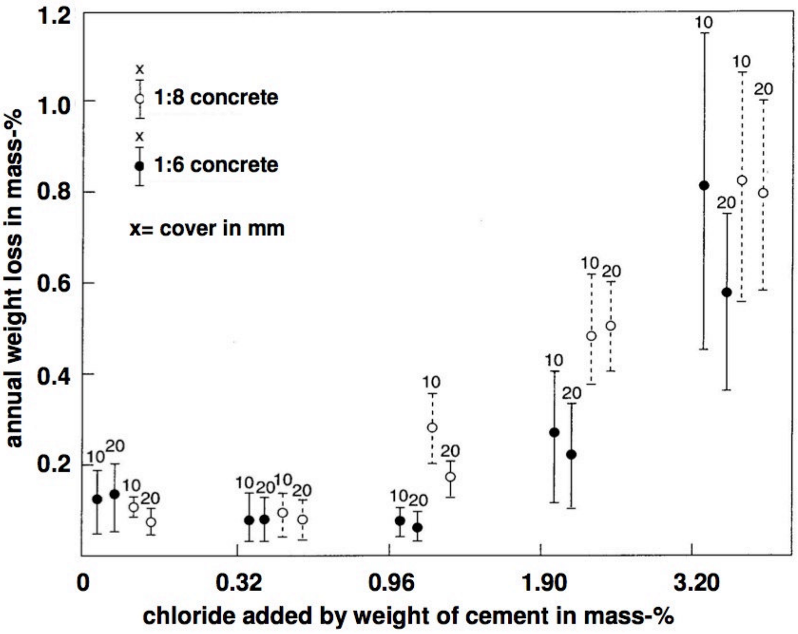


Fig. 5.2.a: Weight loss of shot-blasted unalloyed steel with respect to chloride content of concrete

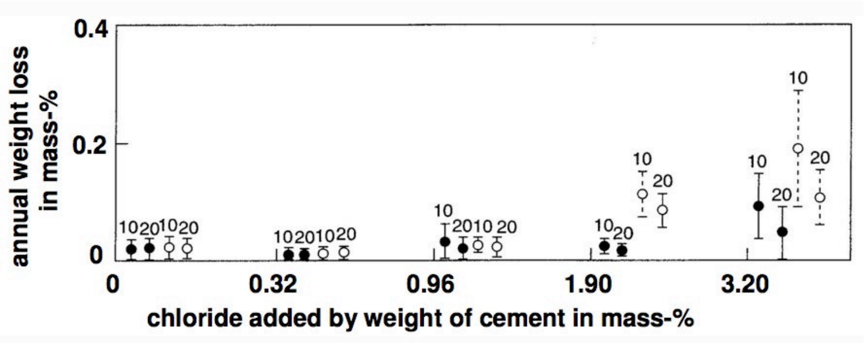


Fig. 5.2.b: Weight loss of type 430 ferritic steel with respect to chloride content concrete

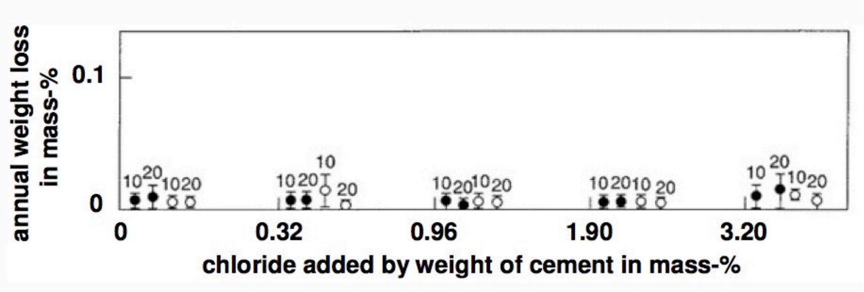


Fig. 5.2.c: Weight loss of type 316 austenitic steel with respect to chloride content of concrete

In spite of the high corrosion resistance of the austenitic type 1.4301, recommendations were made that alloys with molybdenum (1.4401 and higher) should be used in chloride-contaminated conditions to minimise the risk of corrosion, especially where high chloride contents and carbonation to the full depth of cover were anticipated [29].

Investigation 2 [30]

In these tests, mats of 12 mm diameter bars of unalloyed steels and stainless steel type 1.4301 (X5CrNi 18-10) were cast into concrete slabs, using a 0.50 water-cement ratio, 260 kg cement per m^3 of concrete and covers of 25 to 50 mm. To increase the rate of chloride penetration into the concrete, a 15 % sodium chloride solution was used for ponding the specimens. The slabs were ponded for 4 days at 16 to 27 °C, rinsed and dried for 3 days at 38°. This process was repeated for 48 weeks. The ends of upper and lower mats of the steel bars were electrically connected so that the flow of macrocell corrosion current between the anodic top bars to the cathodic bottom mat could be measured.

The conventional black bar generated an average maximum corrosion current density of about 10 $mA \cdot m^{-2}$ with respect to the steel surface area, and became severely corroded. Cracking of the slabs was common. The slabs containing stainless steel exhibited no measurable macrocell corrosion current. After the 48 weeks of testing, the bars were found to be free of any corrosion. The total soluble chloride at the level of the bars with the 25 mm cover after testing was 2.1 mass-% related to weight of cement.

Investigation 3 [31]

A 4.5 year accelerated corrosion test was undertaken to assess the behaviour of a chromium alloyed ferritic steel X3Cr12 (analysis similar to steel type 1.4003). Plain descaled chromium steel bars and mild steel bars were encapsulated in chloride free concrete prisms and exposed to a simulated severe marine climate. The concrete cover was 12 or 25 mm; the concrete was of medium or poor quality.

After the exposure, examination of the prisms containing mild steel showed spalling of the concrete. A comparison of the bars showed severe pitting of the mild steel and negligible corrosion of the X3Cr12. It was stated that ferritic stainless steel with 12 % of chromium might be the best choice in moderately aggressive environments where the higher resistance of the more expensive austenitic stainless steels is not necessary.

The authors try to give an explanation with regard to the non corresponding results of corrosion of ferritic steels of investigations 1 and 3. They suggest that the initial presence of chlorides in the concrete mix in investigation 1 may have hindered the formation of a passivation film on the ferritic steels (these conditions are more extreme than any likely service conditions).

Investigation 4 [32]

The main purpose of this test was to determine the susceptibility of stainless steel reinforcement to crevice corrosion. It was feared that the concrete/stainless steel interface would provide a narrow crevice, particularly favouring corrosive attack. To this austenitic stainless steel bars type 1.4401 (X5CrNiMo 17-12-2) partly embedded in concrete cubes were exposed to seawater, immersed fully or partially. The corrosion resistance was determined from tests of up to about 12.5 years duration. Unalloyed steel specimens were also tested for comparison.

The austenitic steel specimens showed excellent corrosion resistance during the whole test period. Bars having small areas outside the concrete suffered no corrosion, even after 12.5 years. More protruding bars showed some local corrosion, although insufficient to affect strength or ductility. Crevice corrosion on bars partly embedded in concrete was observed on one of the 42 specimens after more than 12 years of exposure. The results shown by the 1.4401 material were even better than expected in this environment, which was considered to be effect of a beneficial influence from the alkalinity of the concrete.

Investigation 5 [10]

Electrochemical investigations have been carried out on ribbed bars of mild steel and stainless steel type 1.4301 (X5CrNi 18-10) and 1.4401 (X5CrNiMo 17-12-2), with and without welds (MIG/ MAG-welding), in mortar samples. The stainless steels were cold-rolled. No attempts were made to remove any deposits from the steel surface that might have been applied during production or welding. The effect of mixed-in chloride (0 - 8 mass-% Cl^- by weight of cement) as well as ingress of chloride was investigated.

Fig. 5.3 gives the results of the potentiodynamic polarisation to 0 mV_{SCE} for the 1.4301 austenitic and the black steel. This potential was assumed to be a realistic value that might be obtained in the passive state. It may be seen that samples with overcritical concentration can easily be distinguished from samples with sub-critical concentration, as the difference in average corrosion rate was approximately two orders of magnitude.

The corrosion attack on stainless steel was more localised than on black steel. The critical chloride concentration for rebars embedded in chloride-containing mortar was more than ten times higher for stainless than for black steel. However, the corrosion properties of the Cr-Ni-Mo-steel 1.4401 were marginally better than for Cr-Ni-steel 1.4301. Welding reduces the critical chloride concentration to 1/3 - 2/3 of that of the unwelded stainless steels.

These results suggest that unwelded austenitic stainless steel of type 1.4301 bars without molybdenum is sufficiently resistant and therefore suitable for application in chloride environments. In the welded state the steel type 1.4401 should be preferred.

Further reinforced mortar samples with mixed-in chlorides (up to 8 mass-% by weight of cement) without and with stainless steel rebars were stored outdoors for 5 months. After exposure the stainless steel samples were nearly all without any sign of corrosion.

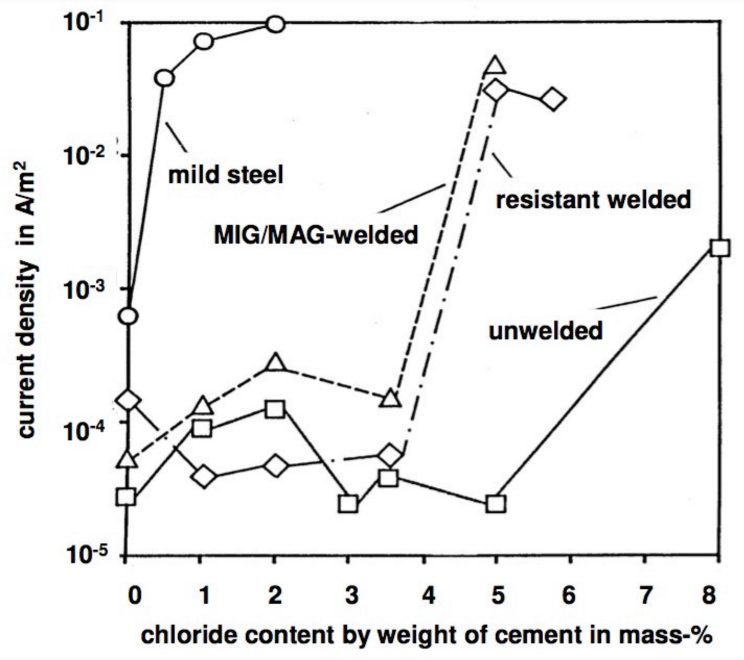


Fig. 5.3: Corrosion current density of steel type 1.4301 versus content of mixed-in chloride 0 mV

Investigation 6 [33]

Stainless clad reinforcing steels of type 1.4301 (X5CrNi 18-10) and unalloyed, galvanised and epoxy-coated steels have been evaluated in a 7-year exposure site programme for corrosion resistance performance in chloride-bearing concretes. The two variables studied were reinforcing material and chloride content of concrete. Bars were cast in prismatic specimens of 0.45 water-cement ratio of good-quality concrete containing three levels of chloride: 0.6, 1.2 and 4.8 mass-% by weight of cement. The specimens were exposed to the environment of Eastern Saudi Arabia.

The results show that unalloyed steel bars had suffered severe corrosion for all three chloride levels, with significant loss of section and rib degradation for 1.2 and 4.8 mass-% chloride-containing concretes. The use of galvanised steel in concretes with high levels of chloride merely delays concrete failure. Epoxy-coated bars performed exceedingly well as corrosion-resistant steel in 0.6 and 1.2 mass-% chloride concretes, as no corrosion and concrete cracking were observed. For the 4.8 mass-% chloride concrete, significant corrosion was observed on the substrate steel under the coating. This caused a systematic break-down of the coating and cracking of concrete. These results indicate that epoxy barrier coatings may have a finite tolerance limit for chlorides.

Among corrosion-resisting steels, the best durability performance was exhibited by the stainless-clad reinforcing bars. After 7 years of embedment in 4.8 % chloride concrete, no sign of corrosion was observed on any of the bars tested.

Investigation 7 [16,34,35]

Electrochemical tests (monitoring the free corrosion potential, measuring the corrosion rate using the linear method and potentiostatic tests) have been carried out to study the corrosion behaviour of traditional austenitic stainless steel types 1.4301 (X5CrNi 18-10) and 1.4401 (X5CrNiMo 17-12-2), and the duplex stainless steel type 1.4362 (X2CrNiN 23-4) in chloride-contaminated concrete with up to 3 % of chlorides (referred to the weight of cement). The tests were conducted on reinforced concrete slabs exposed in the open air. The concrete (w/c = 0.5 and 400 kg $\cdot$ m^{-3} OPC) was of good quality. The stainless steel was as-rolled.

All steel types were in the passive state for the whole range of chloride content considered and there was no substantial difference in their corrosion behaviour. The results of potentiostatic tests confirm the passive state even at +400 mV potentials (with respect to an activated titanium reference electrode).

Investigation 8 [7]

To characterise the corrosion behaviour of stainless steel bars, electrochemical tests to determine the pitting corrosion potential were carried out together with comparative field tests on reinforced elements under typical corrosion conditions.

Determination of the pitting corrosion potential

Table 5.11 shows a list of cold rolled stainless steels investigated with austenitic, ferritic-austenitic or ferritic structures together with the unalloyed steel used for comparison. These materials were tested in the arc-welded and unwelded condition. In general, the weld was not treated; in special cases the oxide layer within the area of the weld was removed by a corrosive paste.

Table 5.11: Listing of the applied materials

No.	material		structure	PRE*	
	steel name	material-number		reinforc. bar	welding material
1	X2CrNiMoN 17-13-5	1.4439	austenitic	33.5	28
2	X2CrNiMoN 22-5-3	1.4462	ferrit.-aust.	31.9	
3	X6CrNiMoTi 17-12-2	1.4571	austenitic	23.6	
4	X6Cr 17	1.4016	ferritic	17	12
5	X20Cr 13	1.4021	ferritic	13	
6	X2CrNi 12	1.4003	ferritic	11	
7	X10CrAl 7	1.4713	ferritic	7	
8	unalloyed	1.0466	ferritic	0	0

*pitting resistance equivalent PRE 1x % Cr + 3.3x % Mo

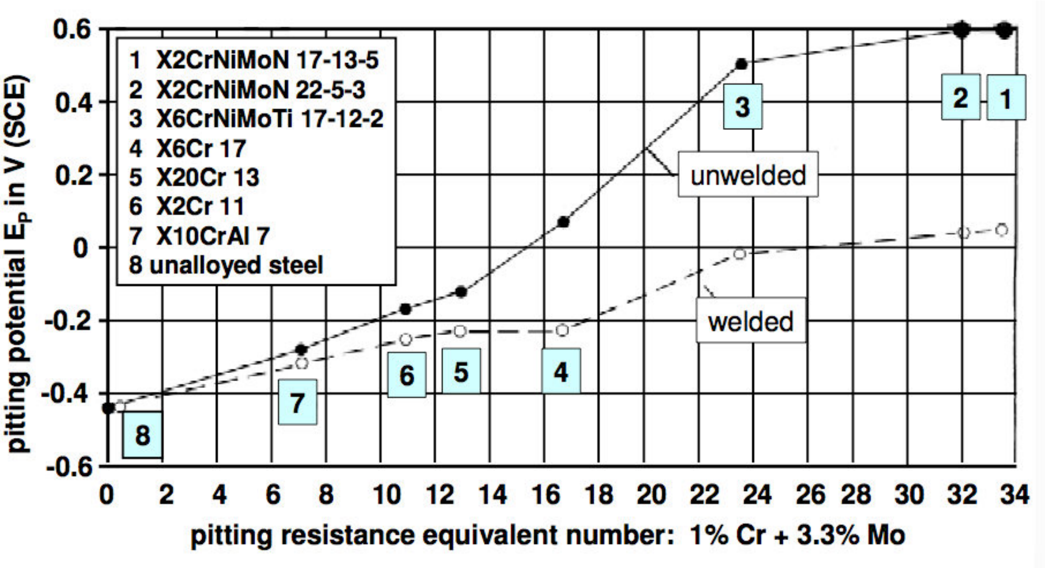


Fig. 5.4: Pitting potential of steel specimens with plain surface in saturated Ca(OH)$_2$- solution with 5 M.-% chloride (potentiokinetic tests)

Potentiostatic investigations on mortar electrodes were performed firstly on plain welded specimens of all steel types. On four typical steels (no. 2, 3, 6 and 8 in Table 5.11), tests were also carried out on cold rolled unwelded and welded ribbed reinforcing bars (compare the details in Table 5.4). Different concentrations of 1.3 and 5 mass-% chloride (related to the weight of cement) were added. One half of the alkaline mortar electrodes (without and with chloride) were artificially carbonated.

Fig. 5.4 gives a short impression of the very different behaviour of unwelded and welded steels in a chloride containing alkaline medium. The pitting potential of the welded specimens becomes more negative, but the difference between unwelded and welded steels, decreases with decreasing alkaline content.

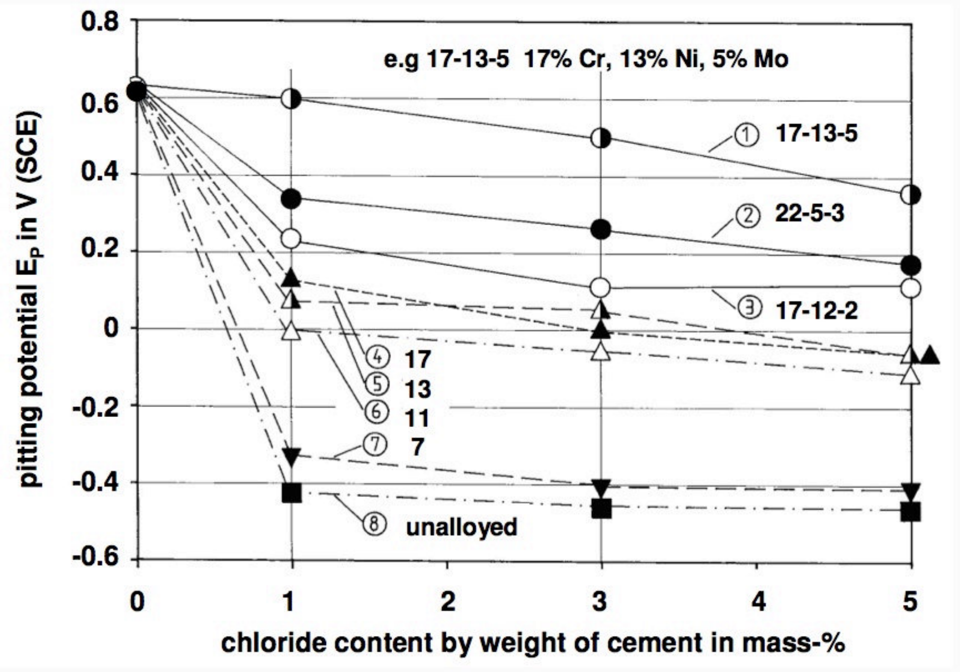


Fig. 5.5: Pitting potential E_P of plain welded steel specimens in PC-mortar-electrodes depending on the steel type and chloride content; potentiostatic test (oxygen evolution potential $E = +600$ mV_{SCE})

Fig. 5.5 and 5.6 show results of the pitting potential of plain stainless steels and one unalloyed steel in the welded state, in alkaline and carbonated concrete respectively, in relation to the chloride content. The numbers beside the pitting potential versus chloride concentration curves refer to the content of chromium, nickel and molybdenum. The following collusions can be drawn:

- The pitting potential decreases with decreasing content of alloying elements (pitting resistance equivalent).Three main groups can be identified:
  - the austenitic and ferritic-austenitic steels 1 to 3 with the highest corrosion resistance,
  - the ferritic types materials 4 to 6 with chromium contents higher than 10 % in a middle range,
  - the ferritic types materials 7 and 8 with chromium lower than 10 % and a low corrosion resistance, comparable to unalloyed steels.

The resistance to pitting corrosion decreases gradually in these three steel groups.

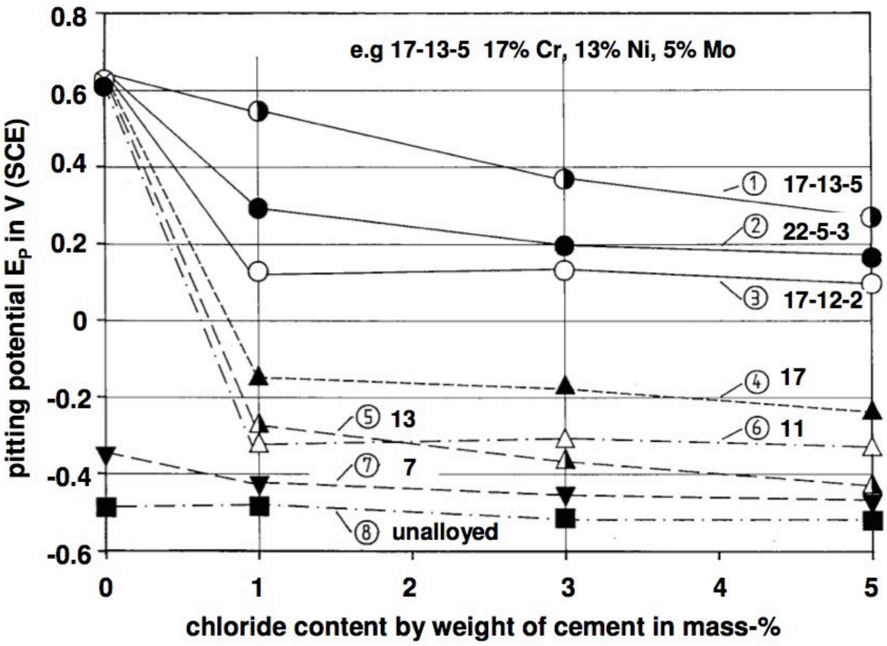


Fig. 5.6: Pitting potential E_P of plain welded steel specimens in carbonates PC-mortar- electrodes depending on the steel type and chloride content; potentiostatic test (t = 24 h), oxygen evolution potential E = +600mV$_{SCE}$

- In the carbonated concrete, free of chlorides, the welded austenitic, ferritic-austenitic and ferritic steels with ≥ 11 mass-% chromium were passive and showed a distinctly better corrosion behaviour than the active materials with ≤ 7 mass-% chromium.

- 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 light-weight concrete or cracked concrete contaminated with de-icing salts, the pitting potential is always shifted to more negative values compared to alkaline concrete with the same amount of chlorides.

Fig. 5.7 shows the results of ribbed steel types 1.4571 (austenitic), 1.4003 (ferritic) and the unalloyed steel after storage in a concrete with 3 mass-% chloride. The following conclusions can be drawn, in addition to those from welded specimens with plain surface (see above):

- In the welded state, ribbed reinforcing bars show a more unfavourable behaviour than plain bars. This is more pronounced for the ferritic steel 1.4003 than for the austenitic steel 1.4571 and more distinct in alkaline than in carbonated concrete.

- Unwelded ribbed stainless steel reinforcing bars in concrete with chlorides show a more positive pitting corrosion potential, E_P, than welded bars. For unalloyed material, no difference between welded and unwelded bars was observed.

After field tests (see below), corrosion can only be expected if the pitting corrosion potential is more negative than -100 mV$_{SCE}$; in this case the necessary condition $E_P < E_{Corr}$ is fulfilled. According to this definition, and the results presented in Fig. 5.7, for the following materials and conditions, corrosion cannot be excluded or can be extremely likely:

- unalloyed steel (unwelded and welded) in carbonated and/or chloride contaminated concrete (chloride ≥ 1 mass-%);
- ferritic, unwelded steel 1.4003 in chloride-contaminated carbonated concrete (chloride ≥ 2 mass-%);
- ferritic, welded steel 1.4003 in chloride-contaminated, alkaline and chloride-contaminated carbonated concrete (chloride ≥ 1 mass-%).

On the contrary no corrosion may occur:

- for austenitic steel 1.4571 (unwelded and welded) under all possible corrosive conditions (carbonated, chloride-contaminated alkaline, chloride-contaminated carbonated);
- for ferritic unwelded steel in chloride contaminated alkaline concrete.

Further investigations showed that the treatment of welded areas of specimens with a pickling paste results in an improvement of corrosion behaviour. For the welded material 1.4003 in alkaline concrete with 3 mass-% chloride the corrosion potential increased from -200 to +600 mV_{SCE}.

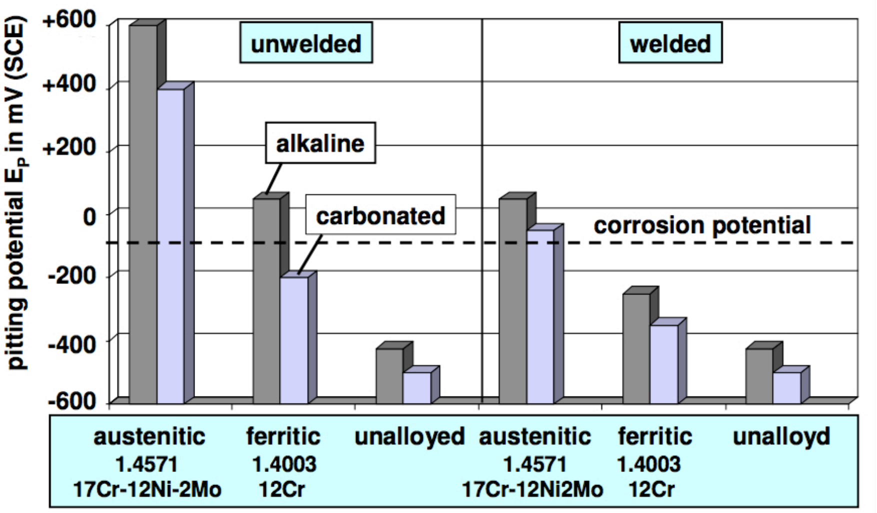


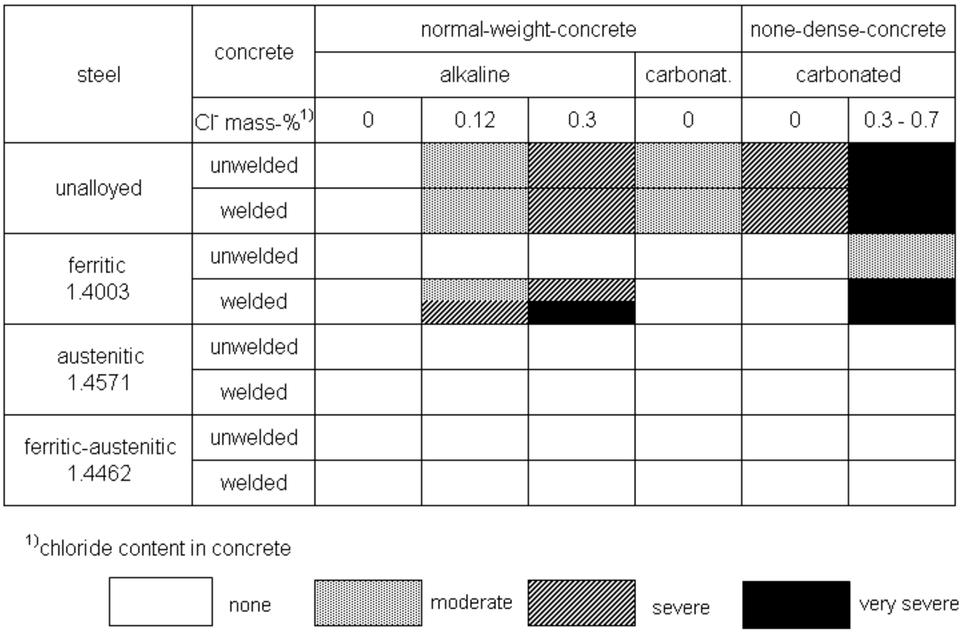
Fig. 5.7: Pitting potential E_P of deformed steel specimens in mortar-electrodes with 3 mass-% chloride depending on the steel type, the presence of welds and carbonation; potentiostatic test (oxygen evolution potential $E = +600\ mV_{SCE}$)

Field tests with reinforced concrete elements

Concrete elements reinforced with cold deformed ribbed bars were exposed in open air for up to 2.5 years. The welded materials consisted of unalloyed and stainless steels of type 1.4003, 1.4462 and 1.4571. There was no treatment of the weld. The concrete types used were a medium normal-weight concrete and two qualities of light-weight concrete (autoclaved gas concrete and permeable concrete). The reinforcing bars had a cover of 1.5 and 2.5 cm. In one part of the normal-weight concrete specimens 1.0 and 2.5 mass-% chloride related to weight of cement was mixed into the fresh concrete. Some elements were additionally carbonated. One part of the light-weight concrete specimens was treated similarly to the conditions of structures in the splash zone of highways where de-icing salt is used.

Fig. 5.8 summarises the results concerning the corrosion attack by means of corrosion degrees based on pitting depth and loss of weight. Areas without and with welds are separated:

- As expected, unalloyed steel bars corrode in carbonated and/or in chloride contaminated concrete. The strongest attack occurred in carbonated plus chloride-contaminated concrete. Cracking and spalling of concrete are common.



steel	concrete	normal-weight-concrete				none-dense-concrete	
		alkaline			carbonat.	carbonated	
	Cl^- mass-%1)	0	0.12	0.3	0	0	0.3 - 0.7
unalloyed	unwelded		░	▨	░	▨	■
	welded		░	▨	░	▨	■
ferritic 1.4003	unwelded						░
	welded		░ ▨	▨ ■			■
austenitic 1.4571	unwelded						
	welded						
ferritic-austenitic 1.4462	unwelded						
	welded						

1)chloride content in concrete

☐ none ░ moderate ▨ severe ■ very severe

Fig. 5.8: Corrosion attack after 2.5 years field tests (survey)

- The unwelded ferritic chromium steel 1.4003 showed a distinctly better behaviour than unalloyed steel. In carbonated concrete (normal- and light-weight concrete) and in chloride-contaminated, alkaline concrete (normal- and light-weight concrete), no attack took place. Nevertheless, in chloride-contaminated carbonated concrete, as for the unwelded steel a reduced pitting corrosion can occur.

- For the welded steel within the weld line chloride produced locally distinct pitting corrosion (Fig. 5.9). The depth of pitting increased with increasing chloride content and was more pronounced in chloride-containing carbonated concrete. For the ferritic chromium steel, the pitting at weld lines was deeper than for unalloyed steel, but the overall general corrosion (loss of weight) was significantly smaller. No cracking and spalling of concrete was observed.

- In all test conditions no corrosion appeared with the austenitic steel 1.4571 and the ferritic-austenitic(duplex) steel 1.4462 whether in the unwelded or welded states.

Investigation 9 [36]

In addition to investigation 3, further tests were conducted on low chromium stainless steel X3Cr12 (chemical analysis similar to steel type 1.4003), austenitic stainless steel types 1.4301 (X5CrNi 18-10) and 1.4401 (X5CrNiMo 17-12-2), high strength carbon steel, galvanised steel and epoxy-coated steel. Reinforced concrete prisms were exposed to the simulated marine environment. Other prisms were exposed to a natural coastal climate, where high temperatures, the proximity to the sea and high humidity result in a severe corrosive environment.

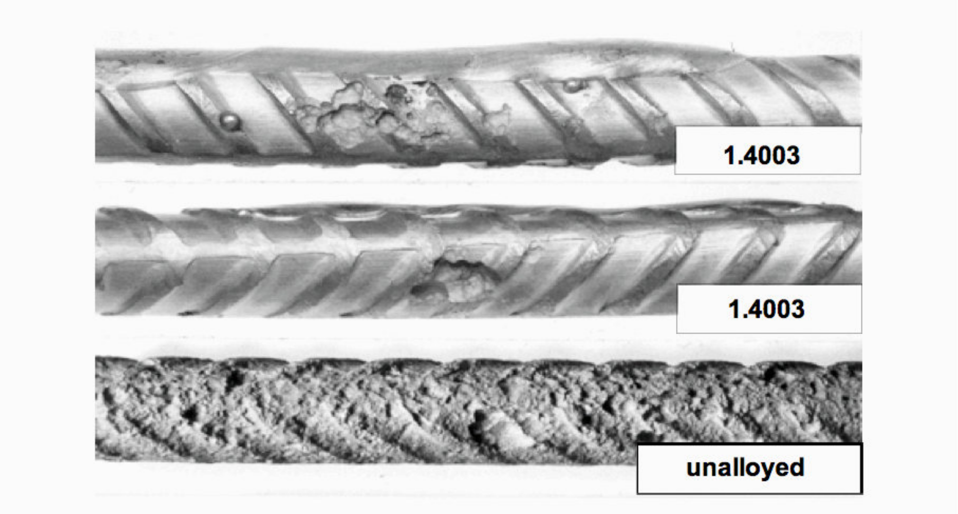


Fig. 5.9: Corrosion of deformed reinforcing bars in concrete (2 years; 2.5 mass-% Cl^-)

After one year of testing in the simulated marine climate, all carbon steel prisms had cracked and stained. Most of the galvanised specimens had also cracked. In contrast, none of the three stainless steels or epoxy-coated rebar prisms showed evidence of cracking, although localised corrosion was observed on the XCr12 stainless steel bars.

None of the prisms stored near the sea exhibited any cracking. However during inspection of bars removed, it was observed that the black bars exhibited some corrosion damage.

Investigation 10 [9]

The localised corrosion behaviour of smooth specimens of austenitic steel 1.4301 (X5CrNi 18-10), 14306 (X2CrNi 18-10), 1.4401 (X5CrNiMo 17-12-2), 1.4404 (X2CrNiMo 17-13-2 and 1.4547 (X1CrNiMoCuN 20-18-6), martensitic steel 1.4006 (X10Cr 13), ferritic-austenitic (duplex) steel 1.4362 (X2CrNiN 23-4) and also carbon steel has been studied, for comparison purposes, in several solutions simulating the liquid present in the pores of both alkaline and carbonated concrete in presence of chloride ions.

Electrochemical tests for evaluating the critical chloride content at a potential of +200 mV vs SCE were performed in solution with pH values in the range 7.6 - 13.9, chloride concentration ranging from 0 to 10 mass-% and temperature of 20 and 40 °C. The adverse effect of pH on the critical chloride content is discussed as a function of stainless steel composition and temperature.

Potentiostatic tests in saturated $Ca(OH)_2$ solution (pH 12.6) of 20 °C at +200 mV_{SCE} showed that corrosion initiated on carbon steel, when a chloride concentration of 0.1 - 0.6 mass-% was reached. The critical chloride content for low-chromium martensitic steel 1.4006 was 2 mass-%. Critical chloride concentrations of 5 mass-% were reached for austenitic stainless steels 1.4306 and 1.4405, and no localised corrosion attacks were observed on ferritic-austenitic (duplex) steel 1.4362, austenitic stainless steel types 1.4301, 1.4401 and 1.4547 up to 10 mass-% chloride concentration (Fig. 5.10).

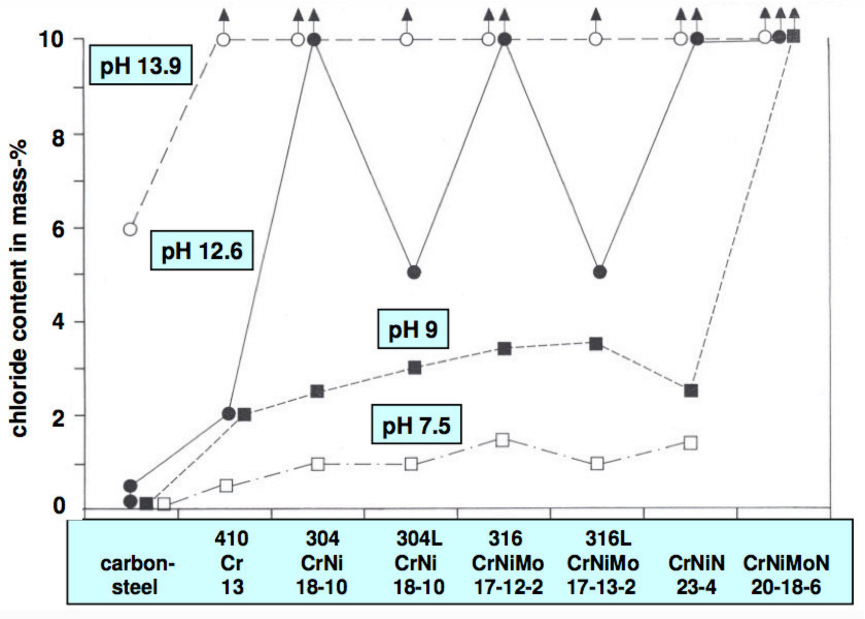


Fig. 5.10 Critical chloride content in pH 7.5 - 13.9 solutions at 20 °C during potentiostatic tests at +200 mV vs SCE

A beneficial effect of alkalinity on chloride-induced corrosion was observed, both on carbon steel and stainless steels. At room temperature, the critical chloride content for carbon steel increased from 0.1 - 0.6 mass-% at pH 12.6 to 6 mass-% in the solution at pH 13.9. All stainless steels had critical chloride contents exceeding 10 mass-% Cl^- in the solution with pH 13.9.

Tests in solutions simulating the carbonated concrete pore liquid showed that stainless steels, although still passive, have a lower resistance to chloride-induced corrosion. The critical chloride concentration decreased, especially for steels with low chromium content. For example 0.5 mass-% Cl^- concentration was enough to promote localised attack on stainless steel 1.4006 at pH 7.5.

The increase of temperature from 20 to 40 °C resulted in a decrease of localised corrosion resistance, except for stainless steel 1.4547 which did not suffer any localised attack at 7.5 - pH 13.9. For example, in the solution of pH 12.6 a reduction of critical content to 4.5 mass-% for austenitic steels 1.4301, 1.4306 and 1.4405 and 3.5 mass-% for duplex stainless steel 1.4362 was found during tests at 40 °C. At this temperature only the austenitic steels 1.4401 and 1.4547 did not show any localised attack up to 10 mass-% chloride concentration.

The results of these tests in solutions simulating the concrete pore solution show:

- Chromium alloyed stainless steels of the type 1.4006 can be used in carbonated concrete, provided a relatively low chloride content (not exceeding roughly 0.5 mass-%) is expected. In alkaline environments, this steel might be useful for chloride contents up to 2 mass-%.

- For higher chloride concentrations (up to 5 mass-%), austenitic stainless steels are necessary at pH values typical of alkaline or carbonated concrete. As far as alloy composition is concerned, austenitic stainless steel 1.4301 and1.4401 and ferritic-austenitic (duplex) steel 1.4362 show a similar resistance to chloride induced pitting corrosion in alkaline and carbonated media. At 40 °C the austenitic steels have a better behaviour than the duplex ferritic-austenitic steel. The very highly-alloyed austenitic steel 1.4547 is justified only under very extreme conditions, i.e. unusually high chloride concentrations and temperatures and carbonated concrete.

Investigation 11 [37]

Severe cyclic wetting and drying tests were conducted on various types of stainless steel bars, and on a single type of stainless steel clad bar. The performance of the bars was monitored by visual inspection and electrochemical polarisation resistance measurements to determine corrosion rates at selected intervals. All bars were 16 mm diameter. Stainless steel types 1.4301 (X5CrNi 18-10), 1.4311 (X2CrNiN 18-10), 1.4401 (X5CrNiMo 17-12-2) and 1.4438 (X2CrNiMo 18-16-4) were tested.

The testing consisted of 1.25 hours of immersion in the salt solution, followed by 4.75 hours of air drying. Two test solutions were chosen to represent conditions found in practice. A 3 mass-% NaCl solution was used to simulate outside salt contamination that could occur prior to the bars being placed into concrete. The second solution was a pH 13.3 solution with NaCl used to simulate bars embedded in salt-contaminated concrete.

The results from linear polarisation measurements are shown in Table 5.12. Table 5.13 shows the ratio of the corrosion rate of each corrosion-resistant material to that of black steel. The 28-day corrosion rate of the black steel in the high pH environment solution was only 8 % of the corrosion rate in the pH 7 solution. In the pH 7 salt solution, the corrosion rate of the stainless steels was approximately 1000 times less than that of black steel, and in the high pH salt solution approximately 100 times less than that of black steel.

No large variations were observed between the corrosion rates for the various grades of stainless steels tested. Corrosion rates were very low, corresponding to the passive state in the high and low pH salt solutions. Thus, it may be reasonable to choose any of these particular materials based upon their physical characteristics, rather than their generally accepted corrosion performance.

Investigation 12 [38]

Long-term natural exposure research using stainless steel reinforcement has been carried out in the onerous climate conditions of the Arabian Gulf region. This region is characterised by aggressive conditions, such as ground and ambient salinity with high temperature and humidity regimes, and even high aridity. Austenitic steel type 1.4401, after natural exposure for 12 years in concrete with a cement content of 220 kg/m^3, poorly cured and with 3.2 % chloride by weight of cement included in the original mix, showed no significant loss in weight due to corrosion. This performance was clearly much better than that of high yield carbon steel reinforcement, which has been known to start corroding after just two years, even in high quality concrete in these conditions.

Table 5.12: Corrosion rates (mA · m^{-2}) determined from linear polarisation measurements on bent bar specimens after 28 days of testing

bar type	solution type	
	rate in mA · m-2	0.3 N KOH + 0.05 N NaOH +3 percent NaCl pH13.3
	28-day corrosion rate in mA · m^{-2}	
black	450.00	35.17
titanium	0.03	0.26
1.4301	0.21	0.28
1.4301 clad	0.22	0.63
1.4311	0.48	-
1.4401	0.43	0.54
1.4438	0.19	-

Table 5.13: Corrosion rate reduction of stainless steel and titanum as compared to black bar

bar type	solution type	
	3 percent NaCl pH 7	0.3 N KOH + 0.05 N NaOH +3 percent NaCl pH13.3
black	1	1
titanum	14350	135
1.4301	2140	130
1.4301 clad	2020	55
1.4311	920	-
1.4401	1040	65
1.4438	2300	-

Investigation 13 [39]

This paper reports the results of corrosion tests on carbon steel and different types of stainless steels embedded in chloride-contaminated concrete with and without accelerated carbonation. Tests were carried out on smooth bars with 10 mm diameter. Tests were carried out on the ferritic stainless steel type 1.4016 (X6Cr 17), the martensitic steel type 1.4006 (X10Cr13) and the austenitic steel types 1.4306 (X2CrNir18-10) and 1.4404 (X2CrNiMo 17-13-2). A series of stainless steel bars were subjected to high temperature oxidation in order to simulate a welding scale (ten minutes at 700 °C so that a bluish oxide scale was produced on their surface).

Concrete was mixed with 350 kg/m^3 of Portland cement, 0.5 w/c ratio and addition of a superplasticizer. The concrete for carbonated specimens (prisms) was of lower quality (260 kg/m^3 of Portland cement, 0.65 w/c ratio). Chloride was added as $CaCl_2$ in the mixing water to 0 to 6 mass-% chloride by cement mass.

Specimens were initially exposed outside and then were moved to a chamber at 40 °C and 95 - 98 % relative humidity. Free corrosion potential and corrosion rate were monitored by the linear polarisation technique.

A chloride content of 1 mass-% by cement was sufficient to initiate the corrosion attack on carbon steel. The corrosion rate increased significantly as the chloride content increased up to 6 % and/or the specimens were moved to the wet 40 °C chamber; then cracking of concrete occurred in a few months of exposure.

All types of stainless steel showed to be passive in carbonated concrete, even at 40 °C.

In alkaline contaminated concrete, the austenitic stainless steels 1.4306 an 1.4404 and the ferritic one 1.4016 showed a negligible corrosion rate, both during the outside exposure and at 40 % and 95 to 98 relative humidity, even in concrete with chloride content up to 6 mass-%. The corrosion resistance of martensitic steel type 1.4006 in chloride contaminated concrete was only slightly better than that of carbon steel, and localised corrosions attacks were observed even at 1 mass-% chloride.

In carbonated concrete, both austenitic stainless steels maintained passive conditions even for a chloride content of 4 mass-% of cement mass regardless of the exposure conditions. A very low corrosion rate was measured on the ferritic stainless steel in carbonated concrete with 4 mass-% Cl^- and wide pitting was observed on its surface.

In alkaline concrete the presence of oxide scale produced at 700 °C led to a slight increase in the corrosion rate of 1.4006 and 1.4306 stainless steel as the chloride content increased up to 4 mass-% by cement mass, although the steel remained passive. No variations in the corrosion rate were observed for 1.4404 stainless steel.

Investigation 14 [40]

The corrosion risk of stainless steel is more pronounced in chloride containing carbonated concrete than in salt enriched alkaline concrete. Doubts had therefore existed that stainless steel is sufficiently safe to be used in cracked concrete of parking decks and walls by the road side contaminated with de-icing salts. Cracks can become carbonated quickly and are open for chloride penetration.

Cracked concrete beams reinforced with welded unalloyed steel, ferritic-austenitic (duplex) stainless steel bars of type 1.4462 (X2CrNiMoN 22-5-3) and austenitic steel 1.4571 (X6CrNiMoT 17-12-2), had been stored and sprayed to replicate the conditions experienced in car parks and also in walls by the road side exposed to chloride containing water. The concrete was of medium quality; the concrete cover was 2.5 and 5.0 cm and the crack widths 0.05 to 1 mm. The cracks were carbonated artificially.

During the test period, the corrosion potential of the steel was measured continuously, to detect the start of corrosion inside concrete cracks. Some beams were opened to reveal the state of the bars.

In the case of unalloyed steel, an essential drop of corrosion potential exists, when the chloride reached the reinforcement in the concrete cracks and the steel became active after 1 to 3 months. Concerning the corrosion resistant reinforcement, the steel remained passive over the whole testing time of 2.5 years.

After opening up some beams, strong corrosion was found in the concrete cracks if the crack width exceeded 0.1 mm in the case of unalloyed steel. No serious corrosion was detected on the highly alloyed steels up to a crack width of 1 mm. Stainless steel reinforcement of type 1.4462 and 1.4571 was found to be suitable for the very unfavourable case of highly chloride contaminated cracked concrete.

5.8.2 Conclusions from research

The information collected in section 5.8.1 has shown that stainless steel offers excellent resistance to corrosion in concrete structures exposed to aggressive environments.

As opposed to carbon steel which is protected by a passive film only in alkaline environments, the protective film which forms on stainless steel is stable in alkaline to neutral and slightly acid environments. Consequently, stainless steels do not suffer general corrosion and will not corrode even in carbonated concrete.

Stainless steel reinforcement has a much higher corrosion resistance against chloride attack and can withstand much higher chloride contents compared to the normal carbon steel; however stainless steels can also be subjected to localised corrosion if the chloride content in the concrete resulting from seawater or de-icing salts exceeds a certain critical value.

Such threshold values depend on the chemical composition and microstructure of the stainless steels, the surface finish and the presence of welding scale, the pH value of the concrete solution and environmental conditions such as humidity and temperature. The intensity of the pitting corrosion increases with increasing chloride content. Carbonation of the concrete will lead to a significant reduction in the critical chloride concentration for pitting initiation.

Unalloyed steels commonly suffer from widespread corrosion in chloride-contaminated environments, with spalling of the concrete cover, while in stainless steel only locally concentrated attack may occur. It was noted that a corrosion attack on a not sufficiently resistant type of stainless steel develops differently than on black steel. On stainless steel, the attack does not spread in the same way as on black steel, but grows more like a pinhole attack. This might lead to a quick reduction in the cross section, and consequently in the load bearing capacity, if corrosion occurs under extreme conditions, particularly if the stainless steel is not highly alloyed enough with respect to the surrounding environment.

Depending on the actual corrosion attack, ferritic or austenitic steel, as well as ferritic-austenitic (duplex) steel, can be used. The corrosion resistance increases in the sequence:

unalloyed		
ferritic	e.g.	Cr12 .... Cr17
austenitic	e.g.	CrNi 18-10
ferritic-austenitic	e.g.	CrNiN 23-4
austenitic	e.g.	CrNiMo 17-12-2
ferritic -austenitic	e.g.	CrNiMoN 22-5-3

These steels used as concrete reinforcement will not corrode at all provided they are selected in accordance with the expected conditions.

The corrosion properties appear to be extremely dependent on the state of the steel surface. In particular, all scale and temper colours can aggravate pitting corrosion and therefore the usual welding procedure will lead to a significant reduction in the corrosion resistance; it reduces the level of chloride contamination at which corrosion can take place. This problem can be overcome by using a more highly alloyed the steel or by removing mill-scale and temper colours by pickling or shot blasting. However all studies also indicated that there was no corrosion of welded molybdenum alloyed steel type 1.4571 and 1.4462 steel under practical conditions of strongly chloride-contaminated, uncarbonated and carbonated concrete (chloride concentrations up to 5 mass-% and higher).

Fig. 5.11 summarises the results of the literature in section 5.8.1 and illustrates the corrosion degree based on pitting depth and loss of weight. Areas without and with welds behave differently:

- As expected, mild steel bars corrode in carbonated and/or in chloride contaminated concrete. The strongest attack occurs in concrete which is both carbonated and chloride-contaminated; cracking and spalling of the concrete specimen are common.

- The unwelded low-chromium ferritic steel of type 1.4003 shows a distinctly better behaviour than unalloyed steel when embedded in carbonated or in alkaline concrete containing low chloride levels. The critical chloride content for pitting corrosion is about 1.5 to 2.5 mass-% depending on state of surface, type of cement (pH value of pore liquid) and concrete quality. However, at higher chloride contents, this steel suffers pitting attack, which is concentrated at a few points on the surface. The tendency to concrete cracking is distinctly lower than for corroding unalloyed steel. In chloride contaminated concrete the (unwelded) steel may suffer a stronger attack if carbonation had reached the steel surface.

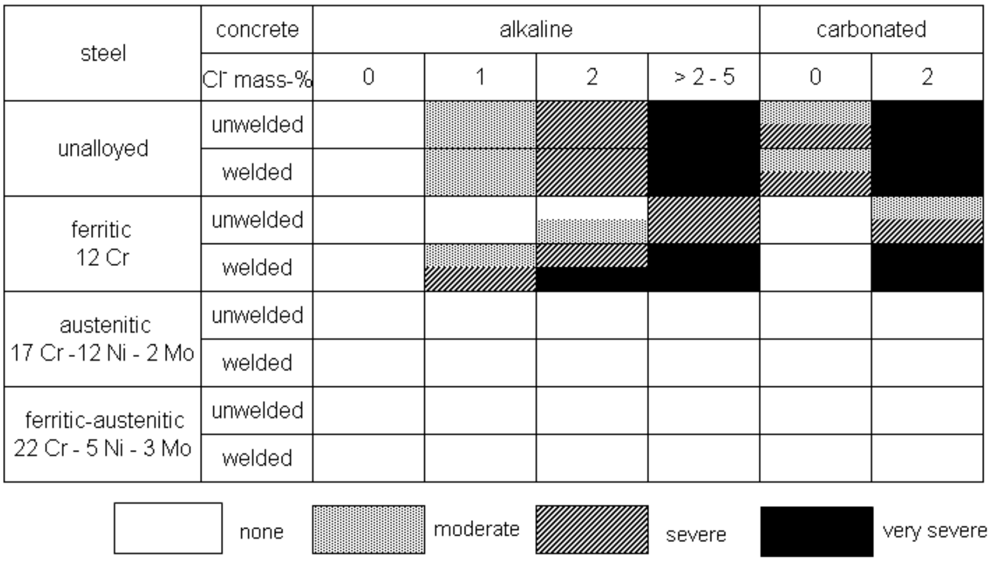
  For the welded steel within the weld line, chlorides in the order of ≥ 0.5 mass-% produce locally distinct pitting corrosion. The depth of pitting increases with increasing chloride content and is more pronounced in chloride-containing carbonated concrete. However, for the ferritic chromium steel the pitting at weld lines is deeper than for unalloyed steel, but the overall general corrosion (loss of weight) is significantly smaller.

- All the higher alloyed stainless steels have a 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 (duplex) steel CrNiMoN 22-5-3 (1.4462). These properties are also maintained at the highest chloride levels that appear in practice and when these steel types are welded.

  The ferritic-austenitic (duplex) steels offer even better properties. These materials may provide a suitable solution to the problem of concrete structures requiring re-bars with high mechanical strength and good corrosion resistance.

  The corrosion properties of austenitic and ferritic-austenitic Cr-Ni-Mo steels are better than for Cr-Ni-steels. Some results [27,28] suggest that, within this group of stainless steels, bars without molybdenum are sufficiently resistant and therefore suitable for application in chloride contaminated concrete. Nevertheless, after results of [10], welded bars without molybdenum seem not to be sufficiently resistant and not suitable for application in presence of more than 3 mass-% chloride in concrete (related to the amount of cement).

In conclusion, one can say that ferritic stainless steel with at least 12 mass-% of chromium might be the best choice in moderately aggressive environments (carbonated concrete or exposed to low chloride levels), where the higher resistance of the more expensive austenitic stainless steels is not necessary. Austenitic stainless steel of type CrNiMo 17-12-2 and ferritic-austenitic (duplex) steel CrNiMoN 22-5-3, even in the welded state, proved to give excellent performance in chloride-containing concrete, even at the highest chloride levels that appear in practice. Austenitic stainless steel of type CrNi 18-10 may be satisfactory in many cases under 'normal' exposure to chlorides, and with no welding of the reinforcement. Higher alloyed steels than those types previously mentioned seem not to be necessary, contrary the recommendations made in [5,19,22].



steel	concrete	alkaline				carbonated	
	Cl⁻ mass-%	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	☐	☐	☐	☐	☐	☐

☐ none ░ moderate ▨ severe ■ very severe

Fig. 5.11: Corrosion behaviour of steel in concrete (survey)

5.8.3 Resistance to galvanic corrosion

Stainless steels can be used for complete or partial substitution of carbon steel in new reinforced concrete structures exposed to aggressive environments or when a very long service life is required.

Due to 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. A possible alternative is to use stainless steel 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. Furthermore, in the rehabilitation of corroding reinforced concrete structures, stainless steels are often used in structures reinforced with normal carbon steel and, in such cases, galvanic coupling can occur.

As long as both metals are in the passive state, i.e. not corroding, their potentials will be more or less the same when embedded in concrete and galvanic coupling does not produce appreciable effects. Even if there were to 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 carbon 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 [11,39,41]. Fig. 5.12 shows that the macrocouple current density (increase in corrosion) was almost one order of magnitude lower when corroding carbon steel in 3 mass-

% Cl^- concrete was connected with passive stainless steel, compared to the current density measured during the tests with a passive bar of carbon steel. This means that the increase in corrosion rate of corroding carbon steel embedded in chloride-contaminated or carbonated concrete, due to galvanic coupling with stainless steel, is significantly lower than the increase brought about by coupling with passive carbon steel. Stainless steel has in the absence of welding scale (see below) a higher over-voltage for cathodic reaction of oxygen reduction (the cathodic oxygen reaction is a very slow process) with respect to carbon steel. That means, 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. Therefore, coupling with stainless steel seems to be less dangerous than coupling with passive areas on carbon steel that always surround the area where localised corrosion takes place. Thus, assuming the 'correct' use of the stainless steel, i.e. stainless steel is used at all positions where chloride ingress and subsequent corrosion might occur, the two metals can be coupled without problems.

Nevertheless, a worse behaviour was observed in the presence of a welding scale (see Fig. 5.12). Oxide scale produced at high temperature increases the macrocouple current density generated by stainless steels to the same order of magnitude or even higher than that produced by coupling with carbon steel.

The fact that stainless steel is a far less effective cathode in concrete than 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. Because it is a poor cathode, the stainless steel should minimise any possible problems that may occur in neighbouring corroding and passive areas after repair.

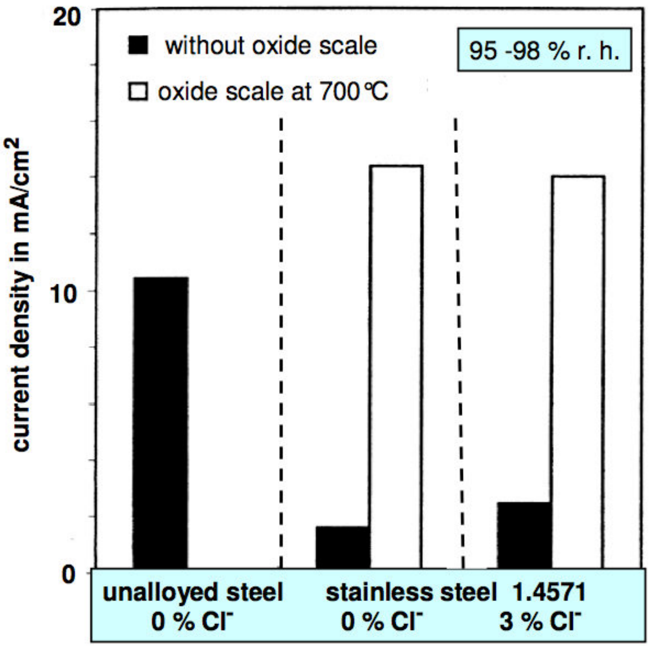


Fig. 5.12: Macrocouple current density in a corroding bar of carbon steel in 3 % chloride contaminated concrete when it was coupled with
- a passive bar of unalloyed steel in chloride free concrete,
- bars of 1.4571 stainless steel in chloride free concrete,
- bars of 1.4571 stainless steel in 3 % chloride contaminated concrete.
Results on stainless steel bars also with the surface covered with oxide scale produced by heating at 700 °C in order to simulate a welding scale [11].

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6 Cost aspects [1]

Cost aspects will be pointed out by way of stainless reinforcing steels. Although the initial cost of stainless steel is significantly higher than that of conventional products (mild steel), their use can often be justified on a life cycle costing basis, also taking into account costs related to future repair and maintenance [2-7]. This means that, in special cases, higher extra cost of the reinforcement may still offer the cheaper and better solution. It is because the above mentioned properties of stainless steel can exclude steel corrosion in reinforced concrete for long periods of service.

Stainless steels are materials of the highest quality, and should be used if reinforced concrete of the highest quality is required. These higher requirements, and the expensive alloying elements contained in the stainless steels, result in a corresponding higher price. Nickel and molybdenum are particularly expensive and those grades having high contents of those elements would be more costly than the leaner alloy compositions. It is therefore necessary to select the lowest steel grade which is adequate for the application, and therefore at the lowest cost. In order to get an idea of the cost level relative cost indices has been given below [8]:

unalloyed		1
ferritic, 12% Cr	(1.4003)	4.9
ferritic, 17% Cr	(1.4016)	4.3
austenitic	(1.4301)	5.5
austenitic	(1.4401)	8 - 11
duplex	(1.4462)	12

The above comparisons are only in relation to alloy content, but subsequent processes may reverse the cost trends. In Germany the price in 2007 of coiled reinforcing wire was:

unalloyed		600 €/t
CrNi 12 (ferritic)	1.4003	2 400 €/t
CrNiMoN 22-5-3 (duplex)	1.4462	4 900 €/t
CrNiMo 17-12-2 (austenitic)	1.4571	5 000 €/t

Because of the lower alloy content, ferritic chromium steel is cheaper than the austenitic Cr-Ni (-Mo) grades currently being used as stainless steel reinforcement in many countries. For many years nobody contemplated using the leaner ferritic grades of chromium steel for reinforcing bars, probably because of adverse reports of their durability that had been published in 1978 [9] and in 1989 [10]. In recent years in South Africa [11] and Germany [12], ferritic steels with 12 and 11 % chromium respectively have been introduced.

The often-stated barrier to use of stainless steel reinforcement is the high initial cost. However, there are many things which must be taken into consideration. The 'intelligent' use of stainless steel can be a very cost-effective option when considering different corrosion protection methods [13]. Stainless steel bar should be substituted for traditional carbon steel rebar only in those critical parts of the structure which are in locations exposed to very corrosive environment. As a result, only a small fraction of the total reinforcement in the splash zones for concrete exposed for marine or de-icing salts, would therefore need to be replaced [14].

There are many applications where the cost of reinforcement for the critical areas of a structure subject to corrosive conditions is only a small part of the total project cost. According to the choice of stainless steel type, the extent of application (partial or total substitution of stainless steel reinforcement for carbon steel), the size of the bar, whether the bars are straight or bent, the complexity of structure and other factors, the price for corrosion protection may be only relatively small and may only be about 5 to 15 % of the total project costs. By contrast, conservative estimates of maintenance and replacement costs come to about 10 times of the cost of additional corrosion protection of the reinforcement (prevention) [7].

Despite higher initial costs, the use of stainless steel can be justified as demonstrated by life cycle cost (LCC) calculations [2,4,7]. In this way the experience gained with the repair and maintenance costs for reinforced concrete structures through their service lives can be taken into account, noting that it is often difficult to provide durable repairs to corroding concrete structures. This is particularly true for marine applications. The technique of life cycle costing was developed for identifying and quantifying all costs, initial and ongoing, associated with a project over a given period.

The following example of a river crossing highway bridge in Schaffhausen/Switzerland, subjected to frequent splashing by de-icing salts, demonstrates the cost effectiveness of the use of stainless steel reinforcement [7]. The primary structural concrete elements in this bridge are the cable pylon and the longitudinal beams of the bridge deck which are exposed to splashing by traffic. It was decided to use stainless steel for the skin layer of reinforcing steel in the vulnerable exposed areas of the longitudinal beams and the bottom 7.6 m of the pylon. The first layer of conventional carbon steel reinforcing bar was covered by 6 cm of high quality concrete, which was considered sufficient cover protection against chlorides over the design period.

Had carbon steel been used for the skin reinforcement of the pylon legs and the longitudinal bridge deck beams, it is estimated that repairs at intervals of 25 years would be required over the entire splashed surfaces. Repairs to the splash zone area of the pylon legs would be an expensive process and involve lane closure and restricted traffic flow. The downtime allowed for in the LCC analysis is 120 days. By using stainless steel for the skin reinforcement, it is expected that no repairs resulting from the corrosion of the reinforcement would be necessary over the design life of the structure.

Table 6.1: Life cycle cost (LCC) analysis summary for the Schaffhausen Bridge [1]

description	carbon steel	stainless steel
initial costs		
material costs	5123 €	55404 €
fabrication costs	0 €	0 €
installation costs	9757096 €	9757096 €
total	**9762219 €**	**9812500 €**
operating costs		
maintenance	0 €	
replacement	160150 €	- 88 €
lost production	1386578 €	0 €
material related	0 €	0 €
total	**1546728 €**	**- 88 €**
total LCC	**11308947 €**	**9812412 €**

Table 6.2: Cost of additional corrosion protection of steel in concrete [4]

corrosion protection	**price (Germany)**	**cost of additional corrosion protection [€/m^2]**	
		100% proportion protected	**50% proportion protected 3)**
unalloyed steel	250 [€/t] 4)	12 1)	
galvanized steel	galvanizing 600 [€/t] 4)	27	20
epoxy-coated steel	coating 440 [€/t] 4)	23	18
stainless steel 1.4571	2875 [€/t] 4)	78	45
nitrite - inhibitor	30 [l/m^3] DCI S 1,1 [€/l]	17	
cathodic protection	design 4 [€/m^2] material 2) 45 [€/m^2] current 1 [€/m^2] monitoring 70 [€/m^2] ∑ 120 [€/m^2]	126	
coating of concrete (crack bridging)	sand blasting 6 [€/m^2] filling 14 [€/m^2] 2 x sealing 15 [€/m^2] ∑ 35 [€/m^2]	41	

1) quantity of steel 0,025 [t/m^2] = reinforcement ratio 1%, diameter: 12 mm

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

3) price of mixed reinforcement

4) cutting, bending, laying 250 [€/t]

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

The Schaffhausen Bridge is considered a key element in the road network. The designers also consider it essential that expensive repair and traffic disruption should be avoided and maintenance should be reduced to the minimum. By adopting the concept of using stainless steel reinforcement for the vulnerable skin area of the splash zones, remedial treatment and traffic disruption will be drastically reduced and maintenance minimised.

Table 6.1 summarises the life cycle costs with regard to initial costs (material and installation) and operating costs (replacement and lost production). The selective use of stainless steel for the area of the reinforcement outlined, increased the initial cost of the structure from 9.76 to 9.81 millions Euros, an addition of only 0.5 % to the total bridge cost. The total life cycle costs over the full designed life time period resulted in a cost reduction of 13 % using stainless steel instead of conventional carbon steel reinforcement. The selective use of stainless steel was considered by the designers to be extremely cost effective.

Using another example, other corrosion protection methods and their additional costs shall also be discussed [4]. A reinforced concrete wall (length 100 m, height 3 m and width 0.3 m) by the road side, exposed to splashing by traffic and chloride-containing water was to be constructed. It was decided to use alternative corrosion protection methods in Table 6.2 in the comparison to conventional carbon steel reinforcing bars. The structural integrity should be maintained for the full design life of 70 years. 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 on the basis of 1999 costs.

The additional costs of corrosion protected reinforcement will, in some cases, vary with the bar diameter, but it is very sensitive to the proportion of protected steel. Therefore, in some cases, it is not likely that the entire reinforcement would be made of corrosion protected steel. For the de-icing salt contaminated wall in Germany, the additional corrosion protection costs were found to be between 2 and 10 times the price of steel which was not protected:

unalloyed steel	100 %
galvanized steel	225 %
epoxy-coated steel	192 %
stainless steel	650 %
nitrite-inhibitor	142 %
cathodic protection	1050 %
concrete coating	342 %

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