SUPPLEMENTARY CORROSION PROTECTION OF REINFORCING STEEL

ZUSÄTZLICHE KORROSIONSSCHUTZMASSNAHMEN FÜR BEWEHRUNGSSTAHL

MESURES SUPPLÉMENTAIRES POUR LA PROTECTION ANTICOR-ROSION de l'acier d'armature.

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SUMMARY

The publication gives a survey of different steel concerning supplementary corrosion protection measures that prevent or retard corrosion. They are proposed and used for new structures but also as repair measures for existing reinforced concrete structures. Besides the performance characteristics also problems with the application are discussed.

ZUSAMMENFASSUNG

Der Bericht gibt einen Überblick über verschiedene, den Bewehrungsstahl betreffende zusätzliche Korrosionsschutzmaßnahmen, welche Korrosion verhindern oder verzögern. Diese Maßnahmen wurden entwickelt und werden genützt in neuen Konstruktionen aber auch bei der Instandsetzung bestehender Stahlbetonkonstruktionen. Neben den Gebrauchseigenschaften werden auch Probleme bei der Anwendung diskutiert.

RÉSUMÉ

Le rapport offre une vue d'ensemble de differentes mesures supplémentaires qui peuvent eviter ou retarder la corrosion de l'acier d'armature. Ces mesures étaient développées et sont utilisées pour des constructions modernes, mais également pour la mise en état des constructions existantes. À côté des qualités du maniement, les problèmes d'application sont également discutés.

1.   INTRODUCTION

Steel in concrete is usually protected against corrosion by passivation of the steel arising from the high alkalinity of the pore solutions within the concrete. A stable oxide layer is formed on the steel surface which prevents the anodic dissolution of iron. Loss of durability in reinforced concrete only occurs if this stable oxide layer is rendered unstable (if depassivation occurs) due to the ingress of chlorides to the steel/concrete interface or carbonation of the concrete reducing the alkalinity of the pore solution at the steel/concrete interface. Durable reinforced concrete therefore must be designed to resist carbonation and to exclude chlorides from any source [1]. Reinforcing steel should be embedded in concrete specified in accordance with current standards. In particular the mix design and minimum cover must be observed and suited to corrosivity of environment. In many cases this will provide sufficient corrosion protection to the reinforcing steel, provided that the concrete is correctly placed, compacted and cured.

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

- 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. by extreme filigree elements);

- special structures have to be erected, e. g. connections between precast and cast in place elements or heat insulated joints between the structure and external structural elements (e. g. balconies);

- non-dense or dense lightweight concrete is designed to reach a required thermal insulation as well as low ownweight;

- structures are exposed to high concentrations of chlorides (e. g. in marine structures and bridge or parking decks due to the use of deicing salts).

In such cases designers may consider modifications to the concrete mix design in order to decrease permeability. Coatings and surface treatments to limit chloride ingress into the concrete, the use of corrosion protected reinforcement and of more corrosion resistant materials for the reinforcement (e. g. stainless steels) and addition of inhibitors to the fresh concrete and cathodic

prevention by impressed current my also be considered. This publication gives a survey of corrosion protection of reinforcement that prevent or retard corrosion and which might be proposed and used for new structures but also as preventive and as repair measures for existing reinforced concrete structures.

2.   EPOXY-COATINGS [1-5]

2.1   Application of coated reinforcement

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 [6]. Later this method has spread also to Canada, 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 deicing 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 USA has increased gradually to about 250.000 tons yearly in 1990. In Europe the application concentrates on single projects.

Standards to epoxy-coating reinforcing steel for example exist in the USA, UK, Germany, Japan and Norway [3].

2.2   Manufacture of the coating

There are two types of epoxy-coatings: liquid and powder coatings. Because of better corrosion protection efficiency [7] electrostatic spraying of epoxy powder to the straight lengths of rebar currently accounts for the majority of coated rebar. After cleaning the steel by abrasive blasting in electrostatic spraying 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 an 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.

With regard to failures in application of epoxy-coated bars in substructure of marine bridges some producer use chromated bars to improve adhesion between steel and epoxy.

2.3 Mode of action

The purpose of the coating is to isolate and insulate the steel from the corrosive environment. The coating act solely as a barrier against the environment. 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 empedes flexibility and bonding of the coating between steel surface and concrete: According to US standard ASTM A 775-81 the thickness of epoxy powder coating in order to fulfil flexibility, bonding and corrosion protection requirements should be between 130 µm and 300 µm.

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 therefore must be free from pores, cracks and damaged areas.

2.4 Properties of coating

Owing to their chemical composition epoxy resins exhibit several physical properties such as high ductility, small shrinkage in polymerisation, good abrasion resistance, good heat resistance and outstanding adhesion on metal surfaces if sufficiently pretreated.

Epoxy resins normally exhibit good durability against solvents, chemicals and water. The long-term durability of most epoxy-coatings in concrete are good. Thin epoxy coatings until 250 µm are not completely impermeable to oxygen and moisture, but diffusion ca be reduced by sufficient thickness and density. 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 [7].

Epoxy-coatings have no electrically but a electrolytical conductivity in the presence of water and/or increased temperatures. Areas beyond the coating can act as anodes and cathodes of corrosion elements if adhesion is removed. But

- the epoxy-coating will not soften or deteriorate in the highly alkaline environment,

- it has an excellent adhesion to a well pretreated steel reinforcement, ensuring no delamination as a result of corrosion forces.

2.5 Corrosion protection behaviour [6-11]

In numerous accelerated corrosion tests on natural exposure epoxy-coated and untreated or in other way protected steel bar reinforcement have been compared. Sound epoxy-coating provided considerable long-term protection to the steel when exposed in carbonated concrete and concrete with a high concentration of chloride. The use of epoxy-coatings free of essential defects guarantees complete protection 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.

Cracks in the concrete did not increase corrosion of epoxy-coated bars with an undamaged coating.

However, the use of coatings in chloride containing concrete does not provide complete protection. 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 defect in the coating. There was very little bonding between the steel an the coating. Film disponding appears to be a consequence of a cathodically controlled underfilm corrosion [10]. 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.

Table 1. Number of concrete specimens with cracks depending on time [8]

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

Table 1 shows typical results of extensive investigations of reinforced concrete beams partly dipped in saturated chloride solution. 100 beams were reinforced with unprotected steel, 100 beams contained epoxy-coated steel according to US-specification (< 6 defects/m, sum of defects < 2 %) and 100 beams were reinforced with epoxy-coated steel and essential more defects in the film as permitted. These results show clearly the detrimental influence of defects on the protection efficiency of epoxy coatings.

2.6 Practical experiences

In the past the applicability of epoxy-coatings to reinforcing steel bars has been investigated with particular reference to bridges [3,6]. The general result reported from USA is that a noticeable reduction in corrosion damage to reinforcement has taken place over the period, in which epoxy-coating has been in use. A field study in Pennsylvania comprised 22 bridge decks after about 10 years service. None of the 11 decks reinforced with epoxy-coated bars showed any visual signs of deterioration. Four of the 11 decks with uncoated bars showed corrosion induced damages.

One failure in performance of epoxy-coated bars has been in the focus of much attention [12]. Five bridges built in the late 1970's and early 1980's linking the Florida keys in less than ten years showed severe corrosion of the substructure in the splash zone and evaporation zone. 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.

The damage included extended 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 disbondment has taken place. Fig. 1 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 yard environment and salt water for a long time caused significant disbonding around existing or introduced coating imperfections (D). This disbondment could develop in the absence of chloride ions. Experiences showed disbondment 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 disbonded coating. A loss of epoxy's insulative properties and macrocell action (chapter 2.7) with cathodic regions in areas of good oxygen availability aggravated the damage.
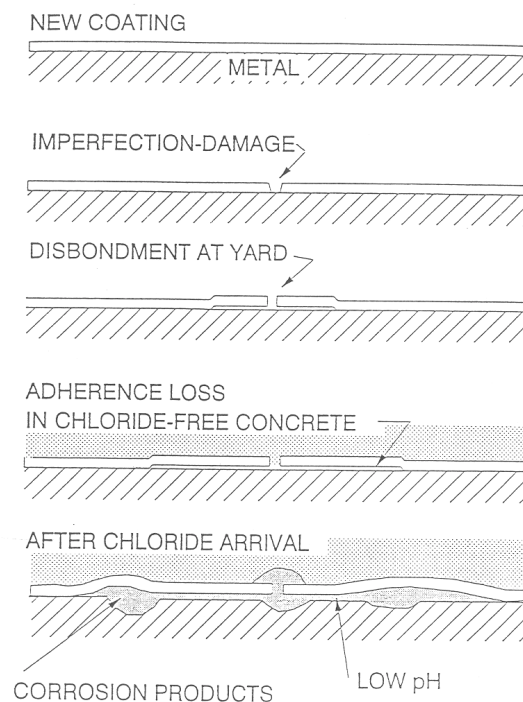

*Fig. 1: Stages in the development of corrosion of epoxy-coated rebar in concrete [14]*

Further in [12] 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 be primarily the result of good concrete quality and thick cover and not necessarily due to the use of epoxy-coated rebar.

2.7 Possible problems with application of epoxy-coated reinforcing steel

- The epoxy-film is not completely free of pores after coating.

- This coating is more fragile than a metallic coating, requiring greater care in handling and use. Epoxy-coated reinforcement therefore must 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 experiences clearly indicate 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 than 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 removed using liquid epoxy. It is advisable to patch only the major defects which cause a corrosion risk. ASTM requires that the sum of damaged areas on a bar should not exceed 2 % of the total surface. The requirements for a good repair make it doubtful that it is achievable on site. Further repaired areas may suffer preferential corrosion attack in concrete structures exposed to aggressive environments [13]. 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.

- 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.

- Welding of the coated bars may generate noxious fumes from the resin. Because of technical difficulties (defects in the weld) the coating on the surface to be welded must be completely removed prior to welding.

- Experiences about epoxy-concrete bond behaviour showed care must be exercised when epoxy-coated reinforcement is used in structural application. Epoxy coating has the effects of reducing bond resistance and increasing slip between reinforcing bars and concrete in comparison to

uncoated bars, with these effects being increased with increasing coating thickness.

- According to several studies on the base of pull-out test, creep-test and repeated bend load coating has a smoothing effect on the surface configuration of indented bars. The thicker the coating is, the greater is this effect. Coated bars with film thickness lower than 250 µm have comparable bond strength to, but higher slip than, uncoated bars.

- The use of coated bars only in the top mat of reinforcement was standard practice in USA and Canada throughout most of the 1980's. Today mostly both layers are coated.
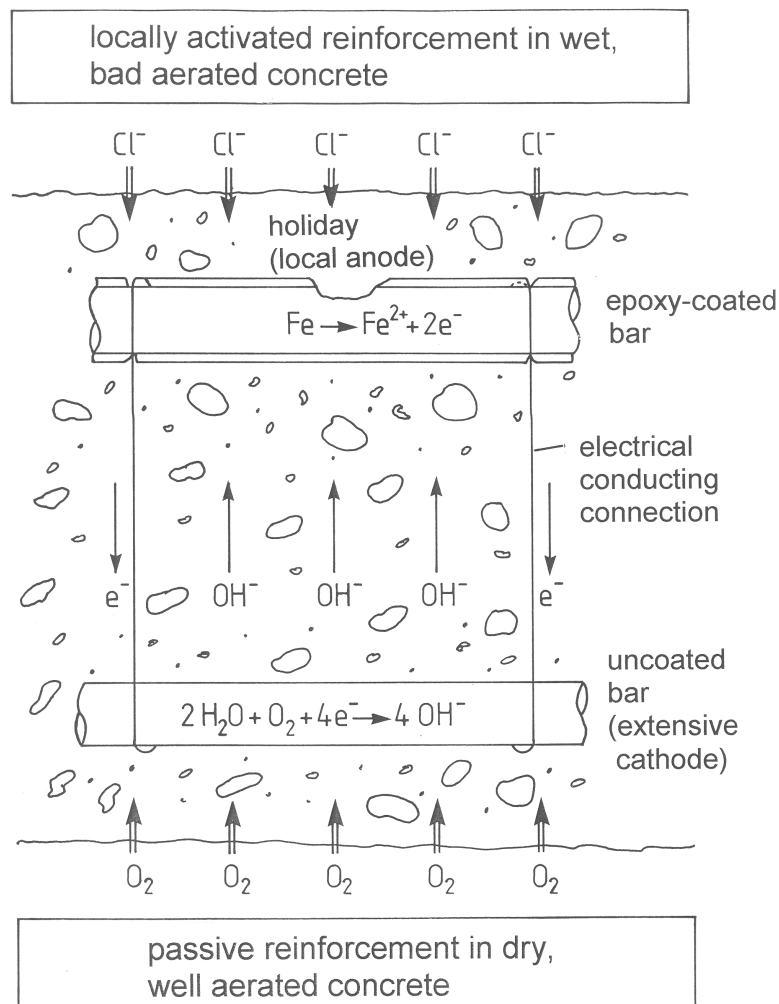
$$i_e(A) = \frac{U_K - U_A}{r_K} \cdot \frac{F_K}{F_K}$$

Fig. 2 Corrosion cell between epoxy-coated bar and uncoated reinforcement (e. g. parking decks)

However, the question arises if there is danger of macrocells developing between coated and uncoated steel in similar application. Fig. 2 shows small anode formed in a coating defect of 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:

– 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 spots of coating defects is embedded in humid (bad aerated), chloride containing concrete and the uncoated steel (extensive cathode) is in dryer (well aerated) still passivating concrete. Then sufficiently high differences of potential arise. High current densities may develop in the area of local faults.

Extensive field tests are reported from FHWA (USA) [2,6,14] comparing three different cases

a) both reinforcing layers uncoated,
b) both layers coated and with damages,
c) upper layer coated and with damages, lower layer uncoated (fig. 2).
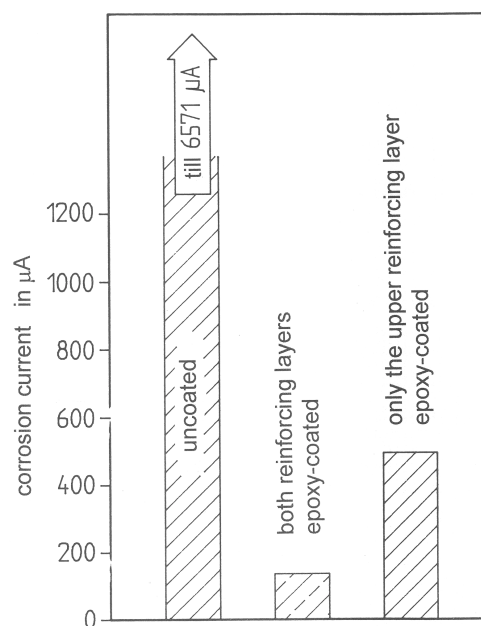

Fig. 3 Corrosion currents depending on the state of coating (FHWA)

Regarding the currents measured to the really existing anodic surface (fig. 3) case c) gives ten times higher corrosion current densities than case a) because in case c) only 1 % of the surface acts as anode. It follows that by using coated reinforcement the formation of macrocells should be considered.

3. HOT DIP GALVANIZING [1,3-5,15]

3.1 Application of galvanized reinforcement

Galvanized reinforcement has been used over the last fifty years in all countries which consumes significant quantities of reinforcement. It seems to be mostly applied in Australia, Bermuda, Netherlands, Italy, UK and the USA. In USA about 2 % of the ordinary reinforcement is galvanized. For Europe the estimate is 1 %. The consumption of galvanized reinforcing steel is increasing yearly. The main application are bridge decks subject to deicing salts, industrial constructions such as cooling towers, chimneys, paper mills and chemical processing plants and a host of buildings of all types. Galvanizing of reinforcement was introduced to improve the service life of concrete structures in tropical and marine environment in America.

Standards of hot dip galvanized reinforcing steel for example exist in the USA, Australia and Germany [3].

3.2 Manufacture of the coating

In the hot dip galvanizing process bars or welded fabrics after pickling and dipping in a aqueous preflux solution to increase the reactivity are immersed in a bath of molten zinc at about 450 °C. In the zinc bath the two metals zinc and iron react in some depth. The layer formed on the surface after leaving are inner zinc-iron alloys bonded metallurgical to the steel base and a outer layer of pure zinc (fig. 4). The iron content of the coating increases from the coated bar surface to the iron coating interface. After the galvanized bars are withdrawn from the bath the thickness of the iron-zinc 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.

As to the steel composition, the silicon content is of the greatest influence. If this is either between 0.02 and 0.15 % or more than 0.3 %, the reactivity between steel and zinc is higher and the alloy layers may become considerably thicker.
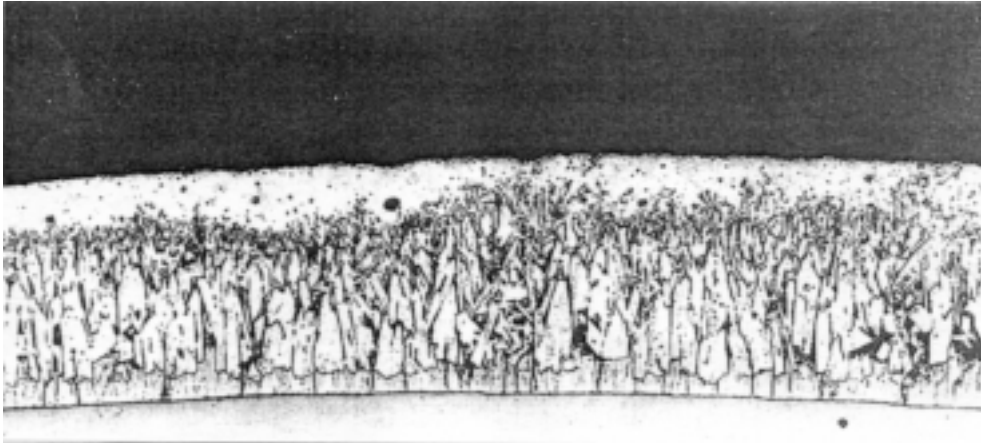
Fig. 4 Structure of the coating of a hot dip galvanized steel

Experience shows that ribbed bars of smaller diameters get thicker coatings of pure zinc. There are two reasons: firstly tin bars cool much faster and secondly they have shorter distances between their ribs. More pure zinc is then taken along from the bath. Ribbed bars automatically get extra thick coating in the transition zone from the bar mantle to the ribs, especially for small diameter bars (fig. 5).
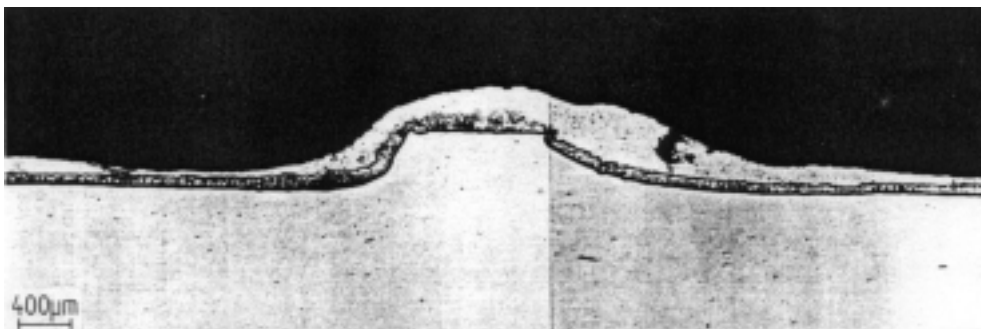

Fig. 5 Thick coating in the rib area of a small diameter reinforcing steel

At temperatures in air higher than 230 °C the zinc crystals anneal through, and there will be no more pure zinc layer. This galvannealing takes place in some minutes. This may be happen if the cooling rate of the bars after withdrawing is low.

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 (see chapter 3.7).

3.3 Mode of action

In a corrosive medium, carbonated and/or chloride containing concrete, zinc coating retards the start of the rebar corrosion, if zinc before creates stable protective film in the alkaline medium concrete. Passivation of zinc reduces the zinc wastage of the normally unstable zinc but it may corrode if the environment is corrosive.

The coating thickness should be as large as possible to render good protection. But thick zinc layers result in less bond to the base steel when subjected to mechanical stresses. It is recommend that the external pure zinc layer of at least 10 µm and a total galvanized layer of at least 80 to 100 µm is necessary to provide suitable protection for use embedded in concrete. A limit of 200 µm is often recommended as maximum.

In a chloride containing concrete zinc may corrode completely at local places. Then the steel after theory may be protected because of cathodic protection by sacrificial dissolution of zinc. 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 [1].

The zinc corrosion products are less expansive and slightly more soluble in the concrete environment than rust. In this way the splitting pressure due to corrosion is reduced.

3.4 Properties of coating

After galvanizing the coating is composed of different iron-zinc layers. In most cases a small layer of pure zinc is the uppermost layer. The intermetallic compounds are very hard and brittle. Therefore zinc-coating has a very good abrasion-resistance but their brittleness can effect the adherence and cracking of the coating when handling galvanized reinforcement. To provide adequate adhesion and to avoid cracking and flaking if impacted or being bent on site the thickness of the iron-zinc layers. should not be thicker than100 to 150 µm. A maximum of insensitivity is guarantied if the thickness of the sum of iron-zinc layers clearly is below 100 µm.

Zinc coatings due to hot dip galvanizing are completely impermeable to gaseous and watery medias. They exhibit a good durability against chemicals and water. The resistance against chlorideions and alkalinity is restricted.

3.5   Corrosion protection behaviour

Alkaline concrete without chloride: In fresh concrete the galvanized coating first dissolves in the alkaline pore water to create a protective layer of high durability. Further zinc corrosion is reduced to a very low rate. A protecting passive layer would be formed at pHs below 13.3 the upper limit for passivation. Passivation is due to the formation of a layer of calcium hydroxozincate on the zinc surface which inhibits further corrosion. The passivating process results in a homogenous zinc depletion of about 5 to 10 μm. A more protective film is produced from pure zinc than from an iron zinc alloy.

In concrete with a cement of exceptionally high soluble alkali content film formation could be inhibited during the setting period and corrosion of the zinc in the hardened concrete will depend on the environmental conditions (humidity, chloride penetration). Above the threshold value at about pH = 13,3 the zinc coating dissolves quickly in an active state with the evolution of hydrogen until the coating disappears totally (fig. 6) [16,17].
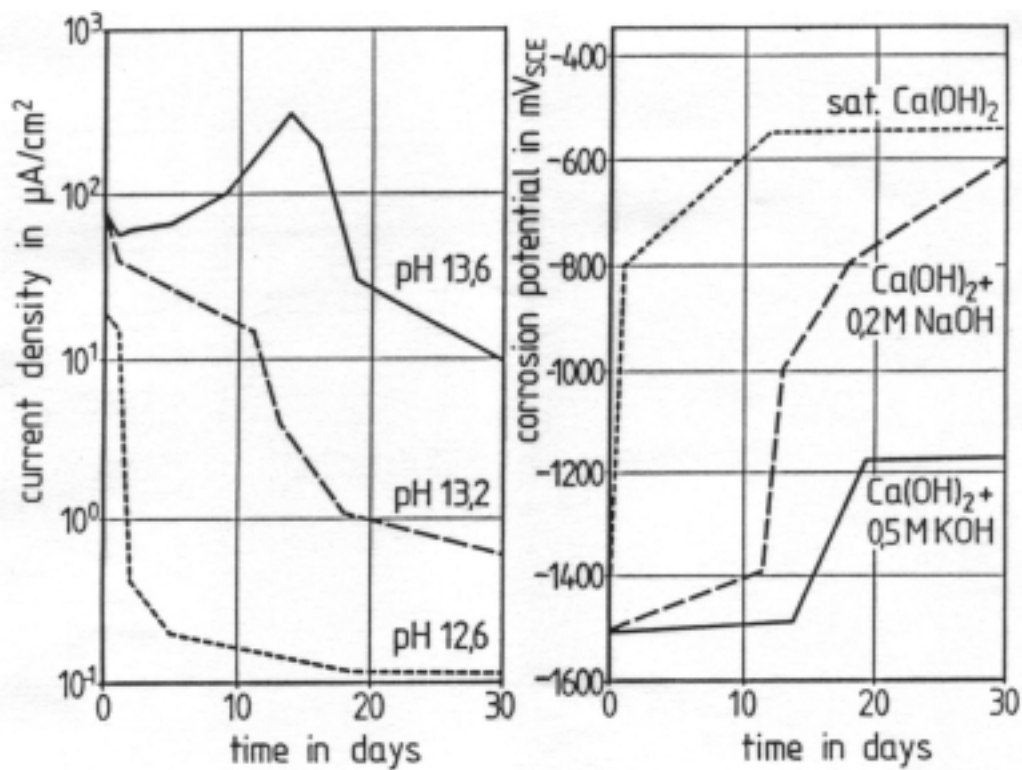

Fig. 6 Corrosion current density and -potential of galvanized reinforcing steel in alkaline solutions with pH 12.6 - 13.2 and 13.6 [16]

Carbonated concrete [5,17-20]: In special laboratory and exposure tests the behaviour of galvanized and not galvanized bar reinforcement have been compared in carbonated concrete. Fig. 7 summarizes the results of this work: In the carbonated concrete the corrosion rate of galvanized steel is significantly lower than that of not galvanized, but something higher than in the alkaline concrete. Zinc coatings remain passive in completely carbonated concrete. This makes galvanized steel reinforcement exceptionally suitable for use in carbonated concrete. Therefore it should be used where a quick carbonation of concrete is to be expected.
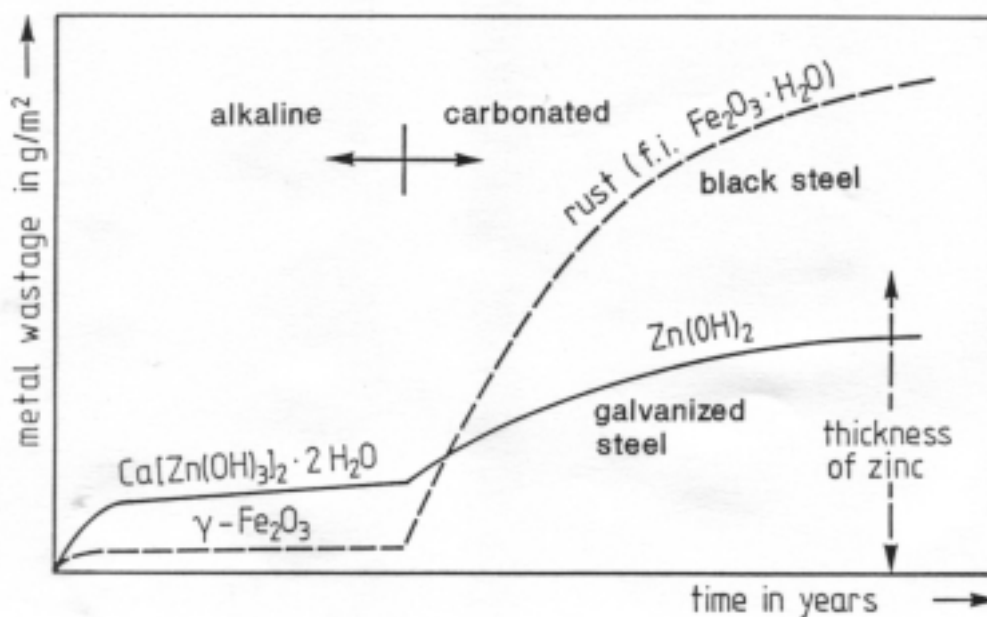

Fig. 7 Corrosion performance of black and galvanized reinforcing steel in concrete (schematically) [1]

Chloride containing concrete [19-24]: Corrosion of galvanized steel in chloride containing concrete is less intense and less extensive for a substantial period of time than that of black steel. The use of galvanized bars therefore guarantees a significant reduction in the rate of cracking and spalling of reinforced concrete containing chloride, respectively deterioration of concrete is less likely to occur.

Though zinc can be depassivated and attacked in the presence of chloride ions the tolerance of galvanized steel to chloride is higher than that of uncoated steel. Long-time marine exposure test of concrete beams reinforced with black and galvanized steel [19,21,23] have shown that the threshold chloride concentration for depassivation of zinc to be much greater than the level required for attack of uncoated steel. If the limit for 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 1.0 -1.5 % for galvanized steel (fig. 8). Consequently galvanized steel in concrete tolerates higher chloride concentration than black steel before corrosion starts. However, the results indicated that galvanized steels are unsuitable for use as corrosion resistant reinforcement in heavily chloride-contaminated concrete.
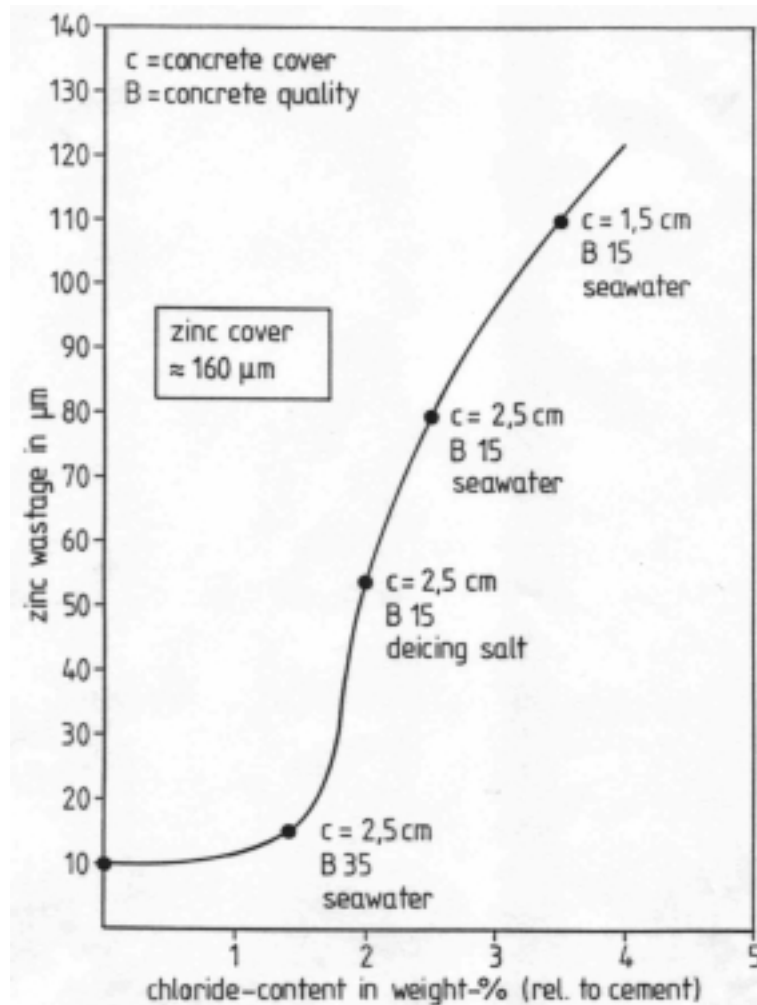
Fig. 8 Zinc wastage of galvanized reinforcing steels after 2.5 years in chloride containing concrete as a function of chloride content [23]

In the presence of chlorides a crack in the concrete cover always represent a special corrosion risk for a galvanized reinforcement [21,23]. In marine environments the presence of cracks represents a shorter way for the access of chlorideions to the steel. The result may be a localized corrosion damage within the crack.

The above mentioned facts depend on further factors as the quality and thickness of the pure zinc layer and the type of cement. 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 when embedded in concrete are less resistant to chloride [15].

The zinc is more unstable at higher pH-values. If there is a high pH-value present, most likely a lower chloride content is sufficient to initiate the corrosion. Regarding the type of cement, the higher the alkali content, the lower the susceptibility to chloride attack should be expected. 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.

3.6 Practical experiences

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 ungalvanized steel (chapter 3.5) and that its performance would not be cost effective galvanized steel has often been used successfully in practice [1,3,15]. But there are other structures in North America where galvanized reinforcement has not performed well and required costly maintenance programmes.

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

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 early failure. But after nearly four years of further laboratory testing in USA and Canada, the poor results have yet to be confirmed. This has led to some controversy.

There are further examples of applications with galvanized reinforcement in North America, Europe, Australia and Japan also in contact with seawater or deicing salts. The structures were mostly intact after some to 20 years in service and the reports give the impression of successful results.

3.7 Problems with the application of galvanized reinforcing steel

- The question is if the process of hot dip galvanizing influences the mechanical properties of the steel itself. Only coldworked steel with a tendency for aging might be embrittled after a certain time. Such steels are not any more in common use.

- Cracks in zinc coating can develop during bending which sometimes result in flaking of the coating. To avoid the risk of such defects the thickness of zinc coating has to be limited (see chapter 3.4); the risk of flaking of zinc coating is lower if a suitable steel is used and the correct galvanizing parameters are met.

- Large areas of cracking or flaking can be repaired with a zinc-rich primer paint.

- For welding all methods used for non-galvanized reinforcement can be used. The zinc-coating influences the welding; this could require some alteration in welding parameters. Is the loss of zinc coating excessive, additional protection by zinc-rich paint is necessary after cleaning the surface in the "burned" area.

- Some user of galvanized reinforcement are afraid that a difference in electric potential of galvanized and not galvanized steel may lead to macrocell action in alkaline concrete. Steel in contact with zinc then tends to accelerate the corrosion rate of zinc. However after the protective layer is formed on the zinc surface and zinc potential rises the potential difference between both metals will be slowed down. The risk of detrimental effects due to galvanic contact disappears. From the authors point of view mixing of galvanized and not galvanized steel may be recommended.

- The development of bond between galvanized reinforcing bar and concrete is dependent both on age of concrete and environment (type of cement). It is an important aspect that the formation of zinc oxide and zincates and the simultaneous hydrogen evolution at the interface between

the bar and the concrete reduce the adhesive bond at early age. The formation of zinc oxide and zincates delay the setting and reduces the early strength of the concrete close to the bar. Hydrogen disrupts the interface between the concrete and the bar. After progress of hydration the strength of the concrete close to the coating surface and also the bond strength increases and bond may be even higher than with not galvanized bars.

- The evolution of hydrogen can be inhibited by passivating agents such as soluble chromates. Soluble chromates are present in most cements to a greater or lesser extent. If the cement contains 0.25 % or more hydrogen evolution is restricted. It has been suggested that this problem can be overcome by adding chromate to the concrete mix or giving the bars a chromate passivation treatment.

- In fresh concrete the pH-value of the pore-water may be between 12 and 14. However the upper limit of stability of zinc is about pH = 13.3 (chapter 3.5). Above this value the corrosion rate of zinc seemed to increase approximately with the increasing pH-values and it exists an ineffectiveness of protection in concrete containing chlorides.

- 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.

4.   STAINLESS STEEL REINFORCEMENT [1,25]

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

The decision on which of these types of stainless steels to use depends on:

– the degree of corrosion protection required,
– cost aspects,
– workability and application characteristics (mechanical properties, weldability).

4.1 Application of stainless steel reinforcement

Stainless steel reinforcement have been used in concrete structures in UK, Italy Germany, Denmark, South Africa and Japan. Typical applications of stainless steel reinforcement are structures which are exposed to very aggressive environments. An increasing amount of austenitic or ferritic-austenitic steel reinforcement is to be found in bridge engineering [26, 27] where influence of deicing salt cannot be excluded. Further these steels are generally located at construction joints or critical gaps between columns and deck. The use of higher quality steels will increase the reliability of multi-storey car park decks which are likely to be contaminated with deicing salts, concrete elements in thermal bath and piers at the sea-coast.

It is intended to use ferritic stainless steel 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.

Standards to stainless steel reinforcement for example exist in the UK, Germany, Denmark and Italy.

4.2 Manufacture of the reinforcement [25]

In principle manufacture of stainless steel reinforcement by hot and cold deforming not distinguish from production of mild steel reinforcement.

One of the initial problems in producing stainless steel reinforcing bars was that the yield strengths of 'as rolled' bars were approximately the same as those for mild steel. Therefore no ferritic or austenitic standard steel in the normal as rolled conditions would have sufficient strength. 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 special heat treatment or cold and warm working will enable high yield reinforcement strength to be reached. 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 high probability that the bars may be further strengthened by cold twisting or cold rolling. These processes can be facilitated by employing a special alloy composition. In this, the carbon and nitrogen contents are limited to avoid hardening after cooling from the austenite phase. The steel retains sufficient strength after cold deforming up to 12 mm diameter.

Acceptable high yield reinforcing bar strengths can be obtained from austenitic stainless steels. Whilst there are other means of increasing the strengths of austenitic stainless steel such as cold working (drawing and rolling, twisting) for the lower dimensions (e. g. 4 to 14 mm), a further attractive method is warm working. Warm working is extremely successful in increasing strength levels of small bars (< 12 mm). An effective solution for large diameter bars up to 40 mm is the combination of using a modified composition (an addition of 0.15/0.20 % nitrogen) and the warm working process.

Owing to their excellent mechanical properties in the as-rolled condition, duplex stainless steels are of interest as materials for reinforcements. In Germany such wires are cold deformed, in Italy they are as-rolled and cold deformed.

4.3 Mode of action

A minimum of about 12 % chromium produces a self-forming passive film of a mixed iron-chromium oxide on the metal surface. An increased chromium content increases corrosion resistance and this may be further improved by additions of nickel, Molybdenum and nitrogen, etc. Chromium, molybdenum and nitrogen are important elements in relation to pitting corrosion. Nickel especially increases corrosion resistance in acid media (further information in chapter 4.5).

Added elements, if present at a sufficiently high level, change the structure of the metal, the corrosion behaviour and other performance characteristics which are structure dependent. Stainless steels that are suitable for reinforcement can be divided into three groups according to their metallurgical structure, namely ferritic, austenitic and ferritic-austenitic. In general, it is convenient to regard the ferritic steels as low carbon plain chromium steels containing less than 17 % chromium. The austenitic steels are low carbon steels containing chromium as well as nickel, the basic type having 18 % chromium

and 8 % nickel. The typical composition of ferritic-austenitic steels (duplex steels) is 22 to 28 % chromium and 4 to 8 % nickel.

4.4   Properties of stainless steel reinforcement

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

4.5   Corrosion behaviour

There are four types of corrosion of stainless steels: general corrosion, intergranular corrosion, pitting and stress corrosion cracking [1]. 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. Therefore, a passivated steel cannot corrode in a medium such as concrete. The passive film is also sufficiently stable if the concrete is carbonated [28].

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

Stress corrosion cracking can occur when appropriate combination of factors such as material, specific environment and stress level are present. The most common austenitic stainless steel type 18 Cr - 8 Ni is sensitive because the nickel content is at a critical value. 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. Stress corrosion cracking is more likely to occur in welded austenitic structures when these are present in carbonated concrete with extreme amounts of chloride at high temperatures. Nevertheless, stress corrosion cracking was not observed in any of the research described in the present report. The most well known examples of failure related

to cracking are concerned with reinforcement which is protruding from concrete [1].

Pitting corrosion is the most common form of corrosion of stainless steels in concrete. Because of the critical role of chloride ions, pitting is a particular problem in concrete with high chloride ion concentrations. The risk of pitting increases with increasing chloride ion concentration, temperature and H^+ ion concentration (or decreasing OH^- ion concentration) and depends on steels composition as well as surface condition. Thus, pitting corrosion is possible on stainless steel bars depending on the type of steel, the state of the surface, the concrete properties (pH value, chloride content) and the potential of the steel. The adverse effect of decreasing pH-value on the critical chloride content as a function of stainless steel composition is shown in fig. 9 [29]. Tests in solutions simulating the carbonated concrete pore liquid showed that stainless steels , although still passive, have a lower resistance to chloride-induced corrosion than in chloride containing alkaline solutions. The critical chloride concentration decreased especially for steels with low chromium content (X 10 Cr 13).
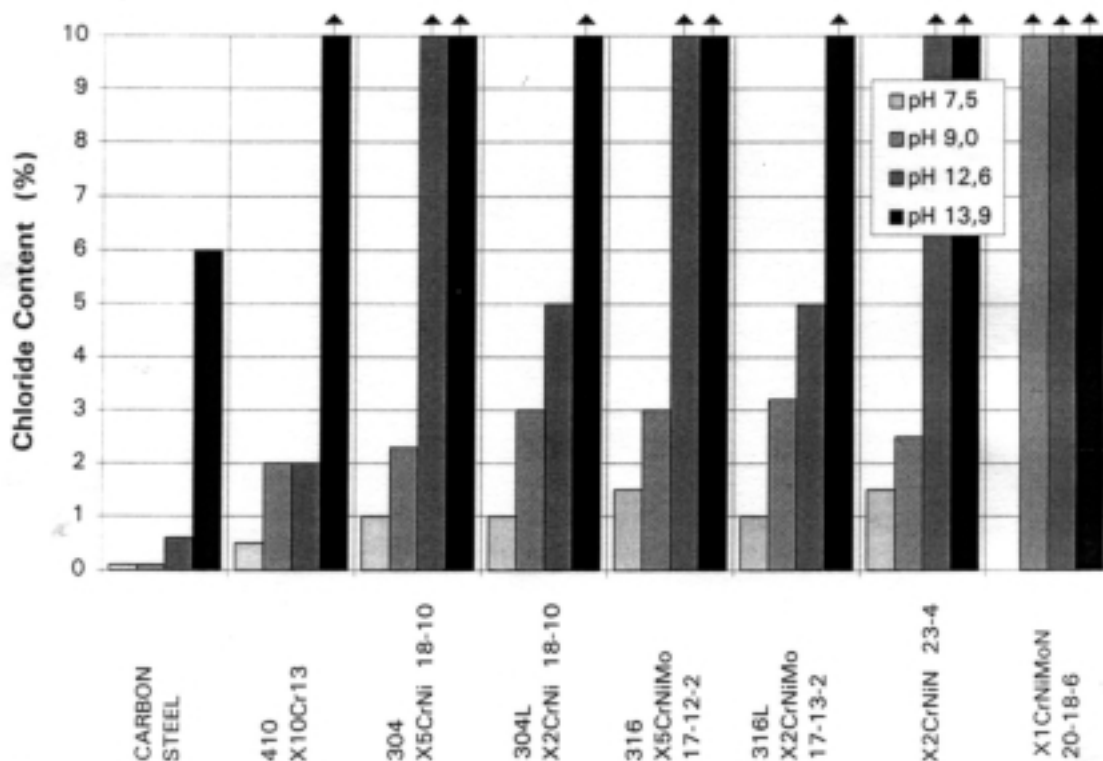

Fig. 9 Critical chloride content in pH 7.5 - 13.9 solutions at 20 °C during potentiostatic tests at +200 mV vs. SCE [29]

The susceptibility to pitting corrosion increases with the decrease of the so-called "pitting resistance equivalent (PRE) number" (1 X %Cr + 3.3 X %Mo + 16 X % N), i. e. 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 pitting resistance equivalent are shown below (the numbers are according to European Standard codes as given in EN 10088):

1.4003	X2CrNi12	ferritic	:11
1.4301 (=304)	X5CrNi 18-10	austenitic	:18
1.4541	X6CrNiTi 18-10	austenitic	:18
1.4401 (=316)	X5CrNiMo 17-12-2	austenitic	:24
1.4571	X6CrNiMoTi 17-12-2	austenitic	:24
1.4462	X2CrNiMoN 22-5-3	ferr.-austen.	:34

Welded bars show a distinctly poorer performance than unwelded bars and the adverse action of chlorides is more pronounced in carbonated than in alkaline concrete. In the case of welds scale and temper colours reduce passivity and can aggravate pitting if not removed. 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 onsite welding of stainless steel.

Many researcher examined the performance of stainless steel reinforcement in electrochemical laboratory studies or in long term exposure programmes under severe marine or simulated marine conditions. In comparison with mild steel bars unwelded and welded stainless steel bars of

– ferritic steel (chromium alloy steel), e. g. X2Cr11 (1.4003) [22,28,30,31],
– austenitic steel (chromium-nickel alloy steel), e. g. X6CrNiTi 18-10 (1.4541) and austenitic steel (chromium-nickel-molybdenum alloy steel), e. g. X6CrNiMoTi 17-12-2 (1.4571) [22,24,28,32],
– ferritic-austenitic steel (chromium, nickel, nitrogen alloy steel), e. g. X2CrNiN 23-4,
   ferritic-austenitic steel (chromium, nickel, molybdenum, nitrogen alloy steel), e. g. X2CrNiMoN 22-5-3 (1.4462) [28,33]

encapsulated in concrete of medium or poor quality were exposed to seawater or chloride containing solutions.

Fig. 10 summarizes the results of literature by means of corrosion degrees based on pitting depth and loss of weight. Areas without and with weld are separated.
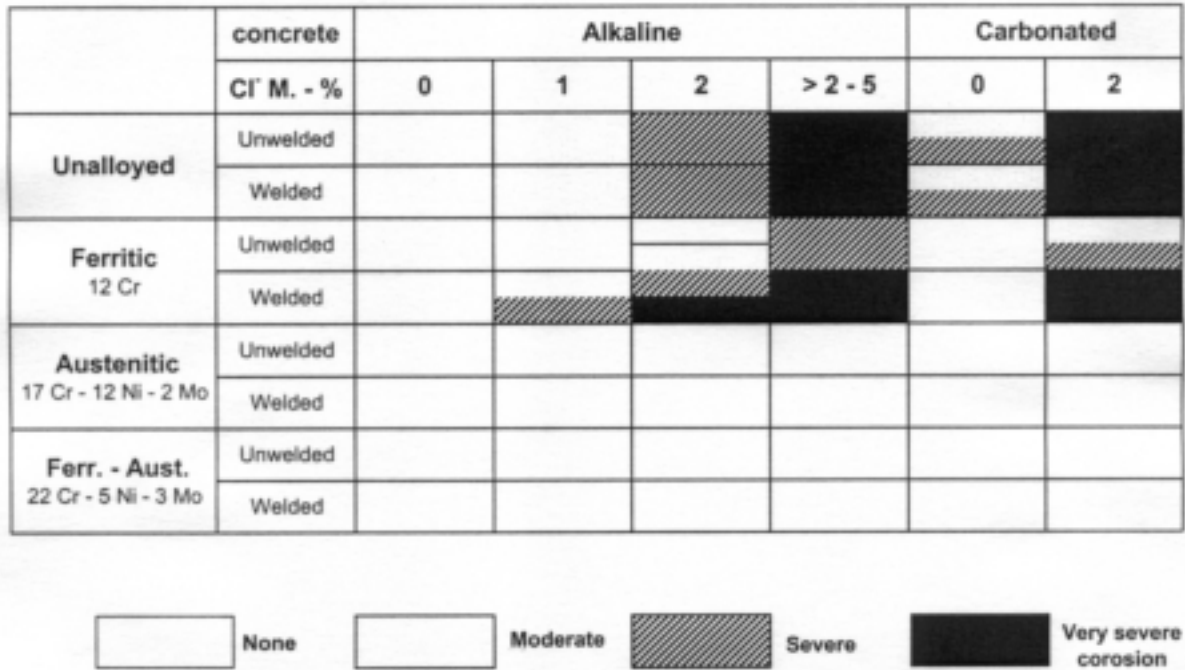
	concrete	Alkaline				Carbonated	
	Cl⁻ M. - %	0	1	2	> 2 - 5	0	2
Unalloyed	Unwelded			Severe	Very severe	Severe	Very severe
Unalloyed	Welded			Severe	Very severe	Severe	Very severe
Ferritic 12 Cr	Unwelded			Moderate	Severe		Severe
Ferritic 12 Cr	Welded		Severe	Severe	Very severe		Very severe
Austenitic 17 Cr - 12 Ni - 2 Mo	Unwelded						
Austenitic 17 Cr - 12 Ni - 2 Mo	Welded						
Ferr. - Aust. 22 Cr - 5 Ni - 3 Mo	Unwelded						
Ferr. - Aust. 22 Cr - 5 Ni - 3 Mo	Welded						

Legend: ☐ None   ☐ Moderate   ▨ Severe   ■ Very severe corosion

Fig. 10 Corrosion behaviour of steel in concrete (survey)

As expected mild steel bars corrode in carbonated and/or in chloride contaminated concrete. The strongest attack occurs in carbonated plus chloride-contaminated concrete. Cracking and spalling of the concrete specimen are common.

The unwelded low-chromium ferritic steel shows a distinctly better behaviour than unalloyed steel when embedded in alkaline concrete containing low chloride levels. The critical chloride content for pitting corrosion is about 1.5 to 2.5 % depending on state of surface, type of cement (pH-value of pore liquid) and concrete quality) [28,29]. However, at very high chloride contents these steels suffer severe pitting attack which is concentrated at few points on the surface. The tendency to concrete cracking is distinctly lower than for corroding mild steel. In chloride contaminated concrete the (unwelded) steel may suffer a stronger attack if carbonation had reached the steel surface.

For the welded steel within the weld line chlorides produced locally distinct pitting corrosion (fig. 11). 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 may

be deeper than for unalloyed steel, but the overall general corrosion (loss of weight) was significantly smaller. Further investigations [28] showed that the treatment of welded areas of specimens with a pickling paste results in an improvement of corrosion behaviour.
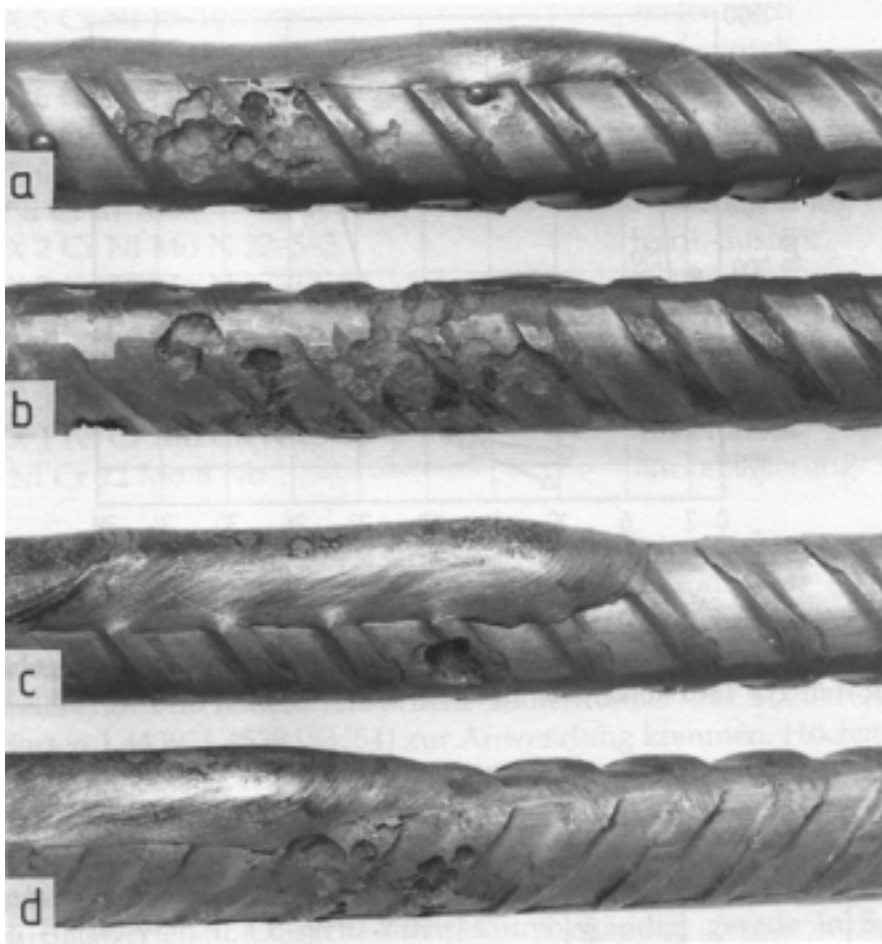

Fig. 11 Corrosion of deformed reinforcing bars in concrete (2 years; 2.5 mass% Cl−)

All the higher alloyed stainless steels showed very high corrosion resistance in all the environments tested:

No corrosion appeared with the austenitic steel CrNiMo 17-12-2 (1.4571) and the ferritic-austenitic steel CrNiMoN 22-5-3 (1.4462) whether in the unwelded or welded states. This was for all conditions within the concrete: carbonated, alkaline and chloride-infiltrated, carbonated and chloride-infiltrated. Analogous to ferritic stainless steel electrochemical studies [28,32] suggest that welding austenitic or ferritic-austenitic steel can effect on the corrosion resistance in chloride bearing concrete and reduces the level of chloride contamination at which corrosion would be instigated. However these studies also indicated that there was no risk of corrosion of welded type 1.4571 and

1.4462 steel under practical conditions of strongly chloride contaminated uncarbonated and carbonated concrete (chloride concentrations up to 5 %). The critical chloride concentration for unwelded rebars in chloride containing concrete is more then ten times higher for austenitic and ferritic-austenitic stainless steel than for black steel [29,32].

However, the corrosion properties of austenitic and ferritic-austenitic Cr-Ni-Mo-steels were marginally better than for Cr-Ni-steels. Some results suggest that within this group of stainless steels bars without molybdenum are sufficiently resistant and therefore suitable for application in chloride concrete.

A consequence of the investigations performed, stainless steel is recommended for special applications of reinforced concrete structures. Depending on the actual corrosion attack, ferritic steel or austenitic steel as well as ferritic-austenitic steel can be used. Stainless steels are resistant in carbonated concrete but may suffer pitting corrosion in chloride-containing concrete.

It was stated that ferritic stainless steel with at least 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.

Austenitic stainless steel of type CrNiMo 17-12-2, even in the welded state, proved to give excellent performance in chloride-containing concrete, even at the highest chloride levels that appear in practice. Austenitic stainless steel of type CrNi 18-10 may be satisfactory in many cases.

Of comparable resistance are the ferritic-austenitic (duplex) steels. These materials may provide a suitable solution to the problem of concrete structures requiring rebars with high mechanical strength and good corrosion resistance.

The use of stainless reinforcing bars based on the above recommendations can exclude steel corrosion in concrete structures for long of service.

4.6 Practical experiences

There exist no extensive long-term experiences with use of stainless steel as reinforcement in concrete. But advantages were realized within numerous applications [27].

4.7 Possible problems with the application of stainless steel reinforcement

- The effect of temperature on the thermal expansion of stainless steel reinforced concrete has not been determined in past investigations. It might be significant and this should be borne in mind if structures in warm areas are to be considered, or in the case of fire.

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

- Because of the very high cost of stainless steel reinforcement it is not likely that the entire reinforcement in, for example a large marine structure, would be made of stainless steel. A possible alternative would be to use stainless only as the outer reinforcement in the splash zone. Stainless steel and unalloyed steel will then probably be in electrical contact and this could lead to a theoretical risk of galvanic corrosion.

As long as both metals are in the passive state their potentials will be more or less the same when embedded in concrete. Even if there should be minor differences in potential, both black and stainless steels can be polarised significantly without serious risk of corrosion. I. e., their potentials will approach a common value without the passage of significant current.

In situations where the unalloyed reinforcement is corroding and the stainless steel is passive, the galvanic coupling will give rise to accelerated corrosion. However, the coupling of corroding carbon steel with stainless steel is generally without risk and is negligible compared to coupling to passive carbon steel which always surrounds the corroding area [34,35]. Stainless steel has a higher over-voltage for cathodic reaction of oxygen reduction with respect to carbon steel. Therefore, the increase in corrosion rate on carbon steel embedded

in chloride-contaminated concrete due to galvanic coupling with stainless steel is significantly lower than the increase brought about with passive carbon steel. 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.

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