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ABSTRACT

In the present work, a large number of publications in connection with critical chloride content has been evaluated. In addition, also a review on available experimental techniques such as the quantification of the chloride content or the detection of depassivation has been worked out.

Many factors are known to influence the pitting corrosion initiation and most of them are also interconnected and variable with time. Thus, any attempts to specify a unique chloride threshold value applicable to a wide range of reinforced concrete structures and environmental conditions are highly questionable. In earlier works, such threshold values have been proposed, *e. g.* the criterion of 0.4% total chloride by mass of cement. It is more and more accepted that such unique values do not exist and that critical chloride threshold values should always be defined by taking into account important influencing parameters such as environmental conditions and properties of the concrete structure.

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Foreword

COIN - Concrete Innovation Centre - is one of presently 14 Centres for Research based Innovation (CRI), which is an initiative by the Research Council of Norway. The main objective for the CRIs is to enhance the capability of the business sector to innovate by focusing on long-term research based on forging close alliances between research-intensive enterprises and prominent research groups.

The vision of COIN is creation of more attractive concrete buildings and constructions. Attractiveness implies aesthetics, functionality, sustainability, energy efficiency, indoor climate, industrialized construction, improved work environment, and cost efficiency during the whole service life. The primary goal is to fulfill this vision by bringing the development a major leap forward by more fundamental understanding of the mechanisms in order to develop advanced materials, efficient construction techniques and new design concepts combined with more environmentally friendly material production.

The corporate partners are leading multinational companies in the cement and building industry and the aim of COIN is to increase their value creation and strengthen their research activities in Norway. Our over-all ambition is to establish COIN as the display window for concrete innovation in Europe.

About 25 researchers from SINTEF (host), the Norwegian University of Science and Technology - NTNU (research partner) and industry partners, 15 - 20 PhD-students, 5 - 10 MSc-students every year and a number of international guest researchers, work on presently 5 projects:

- Advanced cementing materials and admixtures
- Improved construction techniques
- Innovative construction concepts
- Operational service life design
- Energy efficiency and comfort of concrete structures

COIN has presently a budget of NOK 200 mill over 8 years (from 2007), and is financed by the Research Council of Norway (approx. 40 %), industrial partners (approx 45 %) and by SINTEF Building and Infrastructure and NTNU (in all approx 15 %). The present industrial partners are:

Aker Kværner Engineering and Technology, Borregaard LignoTech, maxitGroup, Norcem A.S, Norwegian Public Roads Administration, Rescon Mapei AS, Spenncon AS, Unicon AS and Veidekke ASA.

For more information, see www.sintef.no/coin

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Summary

In the present work, a large number of publications in connection with critical chloride content has been evaluated. In addition, also a review on available experimental techniques such as the quantification of the chloride content or the detection of depassivation has been worked out.

Many factors are known to influence the pitting corrosion initiation and most of them are also interconnected and variable with time. Thus, any attempts to specify a unique chloride threshold value applicable to a wide range of reinforced concrete structures and environmental conditions are highly questionable. In earlier works, such threshold values have been proposed, *e. g.* the criterion of 0.4% total chloride by mass of cement. It is more and more accepted that such unique values do not exist and that critical chloride threshold values should always be defined by taking into account important influencing parameters such as environmental conditions and properties of the concrete structure.

Evaluation of the available literature on critical chloride threshold levels has shown that the published results scatter in a wide range. The reported results span from 0.02 to 3.04% total chloride by weight of binder and thus over two orders of magnitude. On the one hand this results from a lot of different applied measurement techniques and definitions, and on the other hand the large differences can be explained by the complexity and stochastic nature of the initiation of pitting corrosion.

It was found that experimental investigation of the issue of critical chloride content can be performed in a wide variety of possible procedures. The multiplicity of applied methods is the major reason for the difficulties connected with the comparability of the available results. At present there exists no generally accepted or standardised procedure for the determination of the critical chloride content. Not only depassivation of the steel can be detected by various techniques, also the quantification of the chloride content varies and faces some difficulties. The determination of the free chloride content is laborious or even not possible in some cases. Thus, often only the total chloride content is measured. The fact that only chloride that is dissolved in the pore solution is believed to cause depassivation should theoretically favour threshold values expressed in forms that ignore the amount of bound chloride such as the free chloride content or Cl^-/OH^- ratios, *i. e.* these forms should lead to a smaller scatter in results compared to total chloride threshold values. However, the results evaluated in this work do not support this.

From the evaluated reported results on critical chloride content the dominating influences have been identified as follows: 1) The steel-concrete interface: for experiments conducted in synthetic pore solutions, generally lower threshold values have been reported in comparison with studies dealing with mortar or concrete specimens. This can be explained by a Portlandite rich and protecting layer formed at the steel surface in mortar or concrete. 2) The pH value of the pore solution: from solution experiments it is evident that a higher pH value has an inhibiting effect and higher amounts of chloride can be tolerated accordingly. 3) The steel potential: at potentials below -200 mV SCE much higher total chloride threshold values were reported.

A lot of studies have dealt with critical chloride content by quantifying the total chloride content in both mortar and concrete samples or by measuring the free chloride content in solution experiments and mortar or porous concrete. Up to now, there is a lack of information on concrete of higher quality (low w/c ratio, alternative cement types) on the basis of the free chloride content. This may be mainly because of the difficulties in measuring the free chloride content in dense concrete. Moreover, many studies have used mixed-in chloride, although the initial presence of chloride might hinder the formation of a passive layer and thus affect the corrosion behaviour. In the majority of studies the steel bars were prepared (cleaned, sandblasted, etc) prior to the investigation that was

conducted either in a cement based material or in synthetic pore solutions. In many cases the conditions at the steel-concrete interface can thus not be considered as realistic; as was shown this affects the critical chloride content.

Further research is needed, mainly to provide reliable input parameters for service life calculations, which often are conducted by assuming conservative and general chloride threshold values. With regard to the comparability of results reported by different authors it would be of advantage to reach agreement on measurement techniques, mainly the detection of depassivation and the quantification of the (free) chloride content.

1 Background

It is well recognized that the presence of chloride in reinforced concrete can lead to corrosion of the reinforcement by destroying the passive layer on the steel surface (Fig. 1) [1]. Concrete may contain chloride due to admixing during production of the concrete or as a result of penetration from the environment. During production of the concrete chloride may be introduced by using chloride contaminated mixing water or aggregates or by adding chloride containing admixtures (*e.g.* accelerators based on calcium chloride used in the past). Modern design codes and standards for reinforced concrete structures impose restrictions on the amount of chloride that may be present in the fresh concrete mix, *e.g.* according to the European standard EN 206-1 a maximum of 0.2...0.4% chloride by mass of binder is tolerated for reinforced concrete and 0.1...0.2% for prestressed concrete [2]. However, during service life chloride penetrates into concrete structures from the environment in many cases: main sources are marine environment or spray of roads with de-icing salts. Chloride-induced corrosion is thus a frequent cause of degradation of reinforced and pre-stressed concrete structures.

There is a general agreement that reinforcement corrosion in non-carbonated, alkaline concrete can only start once the chloride content at the steel surface has reached a certain threshold value [1,3]. In literature, this value is often referred to as *critical chloride content* or *chloride threshold value*. In this work both terms are used equally.

In European countries as well as in North America it has become common practice to limit the tolerable chloride content to 0.4% chloride by weight of cement, based on earlier work on chloride threshold values [4]. However, much higher (and also lower) amounts of chloride associated with corrosion have been observed in field and laboratory studies. The concept of chloride threshold values appears to be a complex matter. Many factors affect the onset of corrosion, whereas most of them are interrelated and some are very difficult to measure or quantify. It has thus been generally recognised that no unique threshold value exists.

The knowledge of chloride threshold values is of importance for service life predictions when pitting corrosion is the likely failure mechanism. In service life modelling reliable chloride threshold values are required as input parameters: For the design of new structures or for condition assessment of an existing structure, the remaining service life is often considered as the time required to reach the chloride threshold value at the depth of the reinforcement by chloride penetration into the concrete. As soon as this happens corrosion starts and deterioration of the structure may take place. In probabilistic modelling the critical chloride content is a stochastic variable characterized by a mean value, a standard deviation and a type of probability density function.

Whereas more and more, sophisticated mathematical models for service life prediction are developed, there is still a lack of reliable input parameters. Due to the enormous scatter in reported critical chloride contents in literature, often conservative values are used in the range of 0.2...0.5% chloride by weight of cement [5]. In the fib *model code for service life design* [6], the critical chloride content is

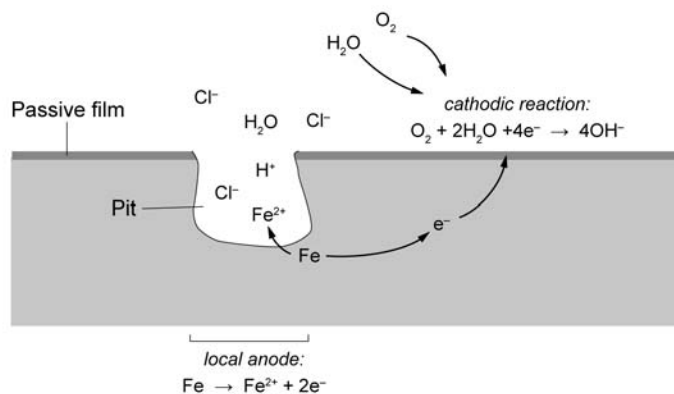


Fig. 1. Schematic presentation of pitting corrosion

defined by a beta-distribution with a lower boundary of 0.2% chloride by weight of cement and a mean value of 0.6% by weight of cement. For this variable, concrete properties and environmental conditions are not taken into account and the variable can be applied to a wide variety of structures. However, the parameter *critical chloride content* as an input factor has been identified to significantly affect the output of probabilistic service life modelling [7,8].

A lot of studies have been undertaken in order to find chloride threshold values in cement based materials. However, the reported results scatter over more than two orders of magnitude (when expressed as total chloride by weight of binder). This lack of agreement can partly be explained by the numerous factors that influence the onset of pitting corrosion; other reasons are different definitions and measurement techniques used or the stochastic nature of pitting corrosion.

Given the numerous investigations undertaken on critical chloride content, some reviews on reported data have been published towards the end of the 1990s [9-15]. In the present state of the art report these reviews are brought up to date by including newer publications and research results. In addition, available laboratory techniques in order to find critical chloride contents have been resumed.

2 Influencing parameters

The critical chloride content for the initiation of pitting corrosion in the case of normal carbon steel is affected by numerous parameters, which often are interrelated themselves. Major factors are the following [3,16]:

- Concentration of hydroxyl ions in the pore solution (pH)
- Potential of the steel
- Presence of voids at the steel/concrete interface

Several other factors may have a direct or indirect influence on the chloride threshold, such as

- Type of cement (chloride binding capacity)
- w/c ratio
- Moisture content of the concrete
- Oxygen content in the concrete

- Chemical composition of the steel
- Surface condition of the steel
- Temperature
- Type of cation accompanying the chloride ion

The variety of factors involved indicates that the concept of critical chloride content faces some difficulties regarding a unique chloride threshold value applicable on a wide range of structures. The results of numerous investigations have shown that the critical chloride content is very variable.

2.1 pH of the pore solution

The presence of Portlandite in the pore solution is the reason for high pH values of ca. 12.6, whereas NaOH and KOH can rise it to values even higher than 13.5. This alkalinity favours the formation of a passive film on the steel surface and is thus important with regard to durability of steel in concrete. The formation of a cement rich layer at the steel-concrete interface stabilises the high pH and contributes to the passivity of steel in concrete [17]. The pH of the pore liquid mainly depends on the type of cement and additions, as well as on the age and environment of the concrete (*e.g.* carbonation). As a result, it is not a constant property and it may change with time. Measuring the pH of the pore liquid for a certain concrete structure is relatively laborious and thus, the accurate pH of a structure is not known in most cases.

Early work by Hausmann [18] in 1967 and Gouda [19] in 1970 – based on steel in solutions simulating the concrete pore solution – indicated that the Cl^-/OH^- ratio is the most accurate way of expressing the chloride threshold level. A log-log relationship between the amount of free chloride that can be tolerated and the concentration of hydroxyl ions was presented in the form of:

$$pH = n \log[Cl^-] + K \quad (1)$$

where $[Cl^-]$ is the highest concentration of chloride in the pore solution that can be tolerated and n and K are constants with n being 0.83 [19]. From this, it can be derived that the ratio $[Cl^-]^n : [OH^-]$ is a constant for initiation of corrosion. However, Gouda pointed out that the linear relationship according to eq. (1) is only obeyed in the range of $11.5 < pH < 13.5$. Hausmann reported threshold Cl^-/OH^- ratios in the range of 0.5 to 1.08 and from probabilistic considerations he suggested that chloride induced corrosion only takes place if the ratio of chloride to hydroxyl activity exceeds a value of about 0.6 [18].

By expressing the critical chloride content as Cl^-/OH^- ratio the inhibitive properties of the concrete are represented by the OH^- concentration in the pore solution and thus, the problem is reduced to only one influencing factor (pH). Although this simplification is questionable, several authors – among them Hausmann [18] and Gouda [19] – confirmed that the pH of the pore solution has a major influence on the amount of chloride that leads to pitting corrosion.

Indirectly, the pH also has an influence since it affects chloride binding. It has been reported that a major part of bound chloride is released as the pore solution pH drops to values below 12.5 and another part is released around pH 12 [20,21]. This was attributed to the dissolution of the solid phases Friedel's salt (calcium-chloro-aluminate) and C-S-H gel. On the other hand, experimental work indicated that there is a competition between chloride and hydroxyl ions for the adsorption sites in the cement paste and thus, the more chloride can be bound (physically adsorbed) the less OH^- ions compete for the adsorption sites, i. e. the lower the pH is [22]. However, it appears that the pH of the pore solution

affects the amount of bound and free chlorides. Variations in pH may occur locally, *e.g.* in voids at the steel-concrete interface; as soon as bound chloride set free, it will be involved in corrosion initiation. Bound chloride can also be released as a consequence of a reduced pH due to carbonation of the hardened concrete.

2.2 Potential of the steel

The electrochemical potential of steel in concrete mainly depends on the oxygen availability and the moisture content at the steel surface. The presence of chloride ions at the steel surface modifies the anodic polarisation curve, primarily by shifting the pitting potential E_{pit} to more negative values (Fig. 2). The electrochemical potential of steel in a certain structure is thus of great importance: If the equilibrium potential E_{corr} is more positive than E_{pit} (which depends on the chloride content), pitting corrosion takes place, otherwise the influence of chloride is negligible. The chloride threshold is thus much higher for steel with a more negative potential.

In a recent study [23] Alonso *et al.* investigated the relation between steel potential and critical chloride content by keeping steel electrodes embedded in mortar and immersed in chloride bearing solutions at various fixed potentials. It was found that the chloride threshold is independent of the potential for values higher than -200 mV SCE, whereas for more cathodic potentials the chloride threshold increases with decreasing potential (Fig. 3).

For structures exposed to the atmosphere, the electrochemical potential of the reinforcement is usually between $+100$ and -200 mV SCE [3]. In this case, the influence of the potential on the threshold level can thus be considered as small. For structures submerged in water, the potential is around -400 to -500 mV SCE and consequently higher chloride concentrations can be tolerated. Apart from environmental factors, the steel can be cathodically polarized by an external current, which also alters the critical chloride content (*e.g.* cathodic protection).

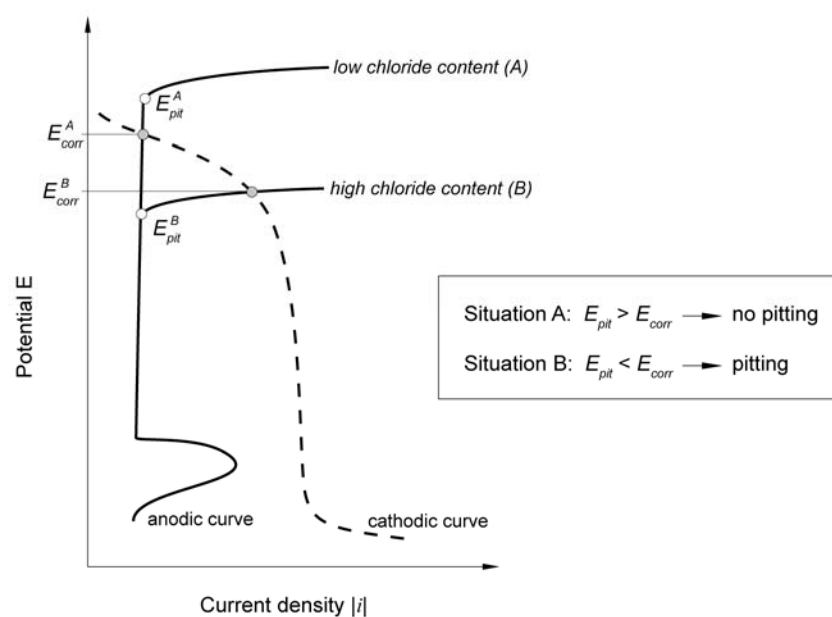


Fig. 2. Influence of chloride on pitting potential

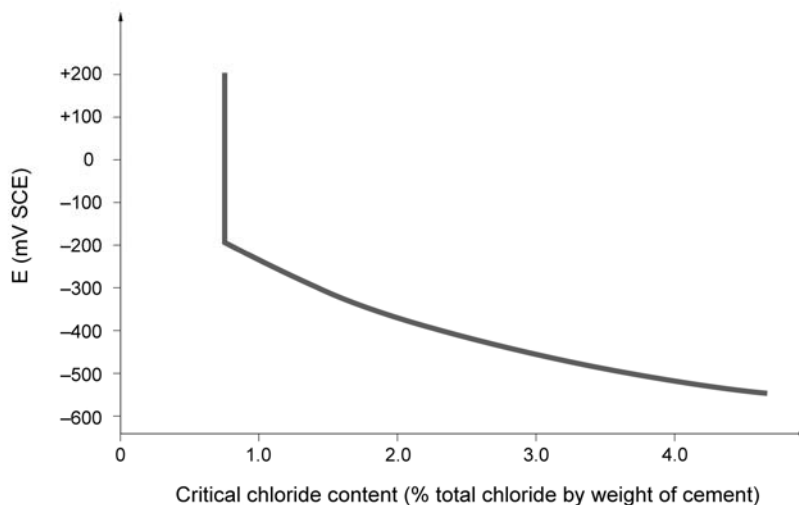


Fig. 3. Potential dependency of the critical chloride content (according to [23])

2.3 Presence of voids at the steel/concrete interface

At the steel-concrete interface, usually a dense lime-rich layer of hydration products can be found, containing a significant quantity of Portlandite [17]. This is of importance since the precipitated calcium hydroxide plays a major role in buffering the pH of the pore solution. The presence of solid material on the steel surface may also act as a physical barrier and restrict the charge transfer reactions (both cathodic and anodic) in certain areas; this may affect the potential of the steel by limiting the area available for oxygen reduction [12,17]. Experimental work has shown that the interfacial zone of segregation rich in Portlandite limits the diffusion of chloride more effectively than the concrete away from the interface [24]. Moreover, it has been reported that the chloride threshold level was significantly lower when the formation of this layer on the steel surface was restricted [25]. Thus, the condition of the interface may have a more pronounced effect on the critical chloride content than variations in the concrete cover or the external environment. As a result of incomplete compaction or a low workability of the concrete, macroscopic voids can be found at the reinforcement. Also the orientation of the rebars with respect to the casting direction may lead to gaps between the steel surface and the concrete [26]. At the concerning sites, the protecting lime layer is weakened or not present at all. The ribs of reinforcement steel may also favor the presence of voids. In this context, it was reported that corrosion preferably occurred at the corners or indents of the profiling [27]. Alonso *et al.* [14] found a higher susceptibility to corrosion for ribbed steel bars in comparison to smooth bars.

In a recent study [28] reinforced concrete beams that had been exposed to salty spray for 14 and 17 years under static load (three-point flexion) were evaluated. It was found that despite rather high total chloride contents (ca. 1.5...2.2% by weight of cement) no corrosion occurred in parts that were subjected to compressive stress, whereas for tensile reinforcement corrosion occurred preferably in the areas most loaded with tension (middle section). This observation was explained by mechanical degradation of the steel-concrete interface (cracks).

To sum up, the condition of the interfacial zone has a major influence on the critical chloride content. However, it is difficult to measure the amount of entrapped air voids and other defects and thus the condition of the interface cannot be quantified.

2.4 Type of cement

The type of cement mainly influences corrosion initiation by determining the amount of chloride that is available in the pore solution as a result of chloride binding and by affecting the pH of the pore solution. Important concrete properties are thus the chloride binding capacity and the effect on the pore solution pH; these will be discussed in the following sections:

2.4.1 Chloride binding capacity

Chloride ions in concrete can be present either in the form of free chloride dissolved in the pore solution or as chloride bound to the constituents of the concrete [29]. It is generally accepted that only the free chloride play a role in the breakdown of the passive layer of the steel and thus in the initiation of pitting corrosion [3]. However, since bound and free chlorides are suggested to be connected by a chemical equilibrium, also bound chloride present a corrosion risk by acting as a reservoir of chloride that might dissolve at altered conditions [20,21,30].

The degree of chloride binding in concrete depends on many factors, among them the amount of cement in the mix, the quantity of the aluminates phases C_3A and C_4AF in the cement, the pH of the pore solution (as presented above), the cation of the chloride salt, etc. Some of the mentioned parameters are determined by the type of cement. Since chloride can be chemically bound to tricalcium aluminate (and to a lesser extent also to the other aluminate phase C_4AF) by formation of Friedel's salt, the C_3A content of a cement remarkably affects its chloride binding capacity. Apart from chemical binding, chloride can also be removed from the pore solution due to physical adsorption to the C-S-H gel. Tang and Nilsson [31] reported that the capacity of chloride binding strongly depends on the amount of C-S-H gel in the concrete, regardless of the w/c ratio and the amount of aggregates. The mechanism of adsorption to the C-S-H gel significantly contributes to chloride binding and may be more important than traditionally assumed [3,30].

2.4.2 Other cements than OPC

Silica fume (SF). The chloride binding capacity of SF containing cements was reported to be lower compared to OPC [32,33]. The partial replacement of OPC with silica fume reduces the amount of aluminate phases and thereby the ability of the cement to bind chloride. Chloride binding in concrete is not only a chemical mechanism, but also a matter of physical adsorption to the C-S-H gel. Since the addition of silica fume leads to a refinement of the pores, the effect of physical adsorption may be more pronounced in SF containing cement. However, it was reported that C-S-H produced by the pozzolanic reaction of silica fume with $Ca(OH)_2$ may have lower chloride binding properties than C-S-H obtained by hydration of OPC [30].

Due to the pozzolanic reaction $Ca(OH)_2$ is consumed and thus, the alkalinity of the pore solution decreases with increasing addition of silica fume [34]. This also affects the chloride binding capacity, since solubility of Friedel's salt increases as the pH of the pore solution is decreased [32]. In addition, the passive state of the steel may be less stable at a lower pH (reduced inhibitive properties of the concrete).

In comparison with OPC, lower critical chloride contents have been reported for SF containing cement [35,36]; in ref. [37] a slightly higher corrosion rates in SF containing

cement was reported. Possible explanations could be the lower hydroxyl concentration in the pore solution and the higher proportion of free chloride due to the lower chloride binding capacity. It has been observed that the Cl^-/OH^- ratio in the pore solution increased considerably with increasing addition of SF [32].

Fly ash (FA). Reinforced concrete specimens that had been exposed to a marine environment for up to four years showed lower chloride threshold levels if they contained FA; the tolerable chloride content decreased with increasing substitution of OPC with FA [38]. Fly ash contains high proportions of active alumina and thus, the use of FA increases the chloride binding capacity of the binder [33,39]. However, it also lowers the pore solution pH: Diamond [40] measured pH values around 13.55...13.60 in the extracted pore solution of specimens containing 30% fly ash, whereas the OPC controls had a pH of 13.75. Kawamura *et al.* [41] found that the addition of FA raised the Cl^-/OH^- ratio in the pore solution. Also Byfors [34] reported a decrease in pH in FA containing cement. Thus, despite increased chloride binding in FA containing cements, the chloride threshold value is expected to be lower compared to OPC as a result of a lower alkalinity of the pore solution.

It has to be noted that the chemical composition of fly ash may vary considerably depending on its origin (type of coal it derives from) and used production techniques. The effect on the concrete properties may accordingly be different.

Ground granulated blast furnace slag (GGBS). If OPC is partly replaced with GGBS the chloride binding capacity of the concrete is increased [33,42,43]. The addition of GGBS to cement increases the aluminate content due to high aluminate levels in GGBS. As a result, more Friedel's salt can be formed as was reported in ref. [42,43]. Thus, the improvement in chloride binding capacity is mainly due to an increase in chemical binding.

The replacement of cement with GGBS decreases the pH of the pore solution: a pH of 12.8 in case of 40% GGBS and 12.4 in case of 60% GGBS replacement in OPC was reported [44].

It must be mentioned that GGBS may contain chloride if quenching with sea water was involved during its production [45]. Thus it is possible that chloride is present in the mix due to use of GGBS.

To sum up, the type of cement primarily influences the critical chloride content by affecting the chloride binding capacity of the concrete and on the pH of the pore solution (Table 1). As these two mechanisms are contrary, it might be difficult to generalise the influence of GGBS addition on the critical chloride content. Gouda and Halaka [46] reported lower chloride threshold values for slag containing concrete specimens in comparison with OPC specimens, whereas Schiessl and Breit found the opposite [47].

Sulfate resistant Portland cement (SRPC). If sulfate ions penetrate into concrete they can react with calcium aluminates to form ettringite. This reaction causes expansion and gives rise to cracking and disintegration of the concrete. Thus, sulfate resisting cements usually contain less C_3A than other cement types. As a result, the chloride binding capacity is reduced. The corrosion risk in SRPC has been reported to be higher than in normal Portland cement [48].

Table 1. Effects of blended cements (in comparison with OPC).

	SF	FA	GGBS
Chloride binding	lower	higher	higher
pH of pore solution	lower	lower	lower

2.4.3 Chloride penetration into concrete

It has to be pointed out that the addition of PFA, GGBS or SF leads to a refinement of the pores of the cement paste and thus to a higher resistance of the concrete against chloride penetration. Also the binding capacities affect the penetration resistance: In cements with a high chloride binding capacity, the ingress of chloride is retarded by removing (binding) chloride from the pore solution. It is well known that a lower permeability of aggressive ions beneficially affects the durability of a structure because more time is needed for the chloride to reach the steel. However, as soon as the chloride penetration front has reached the reinforcement, the initiation of corrosion depends on the factors discussed above. The porosity of the concrete is then of less importance; perhaps an influence could be considered by keeping the concrete resistivity high and thus establishing ohmic control of the corrosion process or by a denser paste around the steel-concrete interface.

2.5 Surface condition of the steel

In many investigations in the laboratory, the reinforcing steel of interest is prepared prior to testing, *e.g.* sandblasted or polished. However, in practice the reinforcement is used “as received” and might be pre-rusted or coated with mill scale. It has been shown that the condition of the steel surface has a significant effect on the critical chloride threshold. Mohammed and Hamada [49] investigated steel bars with various surface conditions such as mill-scaled, polished, brown- and black-rusted and steel bars that were covered with cement paste (pre-passivated) before casting. They found the highest chloride threshold levels for the pre-passivated steel and the poorest corrosion resistance for the mill-scaled steel. Visual observation of split samples showed that brown rust creates a weak physical barrier on the steel surface as some rust separated from the bars and adhered to the concrete. In contrast, black rust forms a strong physical barrier and thus protects the steel. The chloride threshold values were sequenced as pre-passivated > black-rusted > polished > brown-rusted > mill-scaled. Also Mammoliti *et al.* [50] reported higher chloride threshold values for polished steel surfaces compared to ground or as received samples. Li and Sagüés [51] exposed steel bars with different surface conditions in alkaline chloride containing solutions. They investigated steel bars as received (mill scale), sandblasted and pre-rusted and found higher chloride threshold levels for sandblasted bars, although the corrosion rate of the sandblasted steel was higher once corrosion was initiated. Also Manera *et al.* [36] reported a higher critical chloride content for sandblasted steel bars in comparison with steel bars in “as received” condition. Mahallati and Saremi [52] found that the presence of mill scale retards the formation and protective characteristics of the passive layer. Gonzales *et al.* [53] reported that passivation is delayed or even inhibited if reinforcement steel is considerably pre-rusted. It has to be noticed however, that the investigated steel had been pre-rusted by exposure to sea-water and the rust layer thus contained chloride. Certainly, the presence of chloride affects the process of passivation.

2.6 Influence of other factors

Together with the above discussed factors, also other parameters are of importance for critical chloride threshold values. The mechanism of these will briefly be pointed out as follows:

Moisture and oxygen content. Both, water and oxygen are required for the corrosion process and a lack of these can thus limit the corrosion rate. The oxygen content determines the potential of the steel which is an important parameter concerning the

critical chloride content (section 2.2). The amount of water in the concrete pores plays a major role in the distribution between free and bound chlorides and thus determines the chloride concentration in the pore solution. In a rather dry concrete, the electrolytic process is permanently restricted and an increase in moisture content will lead to a higher corrosion probability. In water saturated concrete the corrosion process is inhibited due to lack of oxygen and thus higher chloride concentrations can be tolerated; a decrease in moisture content will allow oxygen to reach the reinforcement more easily and lead to a decrease in critical chloride content.

w/c ratio. The w/c ratio mainly determines the porosity of the concrete and by this the availability of moisture and oxygen at the reinforcement. A higher w/c ratio results in a larger amount of pore water and thus influences the concentration of the free chloride. As there are equilibrium conditions between free and bound chloride, the w/c ratio has also an effect on chloride binding. It also affects the electrical resistivity of the concrete and can thus limit the corrosion process due to ohmic control. It has been shown that the critical chloride content increases with decreasing w/c ratio [27,35].

Chemical composition of the steel. The formation of the protecting passive layer depends on the chemical composition of the reinforcing steel. Normal carbon steel does typically not contain sufficient alloying elements to form a stable passive film at lower pH values or in the presence of chloride ions. However, also the chemical composition of normal carbon steel can vary and might influence the corrosion behaviour.

Type of chloride cation. The corrosion behaviour depends on the type of cation accompanying the chloride ion. If CaCl_2 is added to the concrete mix it behaves as an efficient accelerator of the hydration; compared to NaCl more chloride will be bound within a short time due to the faster hydration [54]. It was reported that CaCl_2 has a much more corrosive effect than NaCl or KCl [55]. This was mainly the result of a coarser pore structure and a lower pH of the pore solution.

2.7 Summary of influencing parameters

Table 2 is based on [12] and summarises the above discussed interrelations. It gives an overview of the effect of various factors on the critical chloride content and also shows that the influence doesn't necessarily have to be the same with regard to the form chosen for expressing the threshold value (which will be discussed in the following sections).

Table 2. Effect of various factors on critical chloride content

Factor	Effect on critical chloride content			References
	total Cl ⁻ % cem wt	Cl ⁻ /OH ⁻ ratio	free Cl ⁻	
Steel properties				
Voids at interface	↓	↓	↓	[25]
Polishing, sandblasting	↑	↑	↑	[49–51]
Steel potential (> -200 mV SCE)	—	—	—	[23]
Steel potential (< -200 mV SCE)	↓	↓	↓	[23]
Concrete and binder properties				
w/c	↓	↓	↓	[27,35]
Chloride binding	↑	—	—	³⁾
pH	↑	↑	↑	[18,19]
SF	↓	↓	¹⁾	[35,36]
FA	↓	¹⁾	¹⁾	[38]
GGBS	↓↑ ²⁾	¹⁾	¹⁾	[46,47]
SRPC (C ₃ A + C ₄ AF content)	↑	¹⁾	¹⁾	[48]
External factors				
Moisture in rather dry concrete	↓	—	—	³⁾
Moisture in nearly saturated concrete	↑	↑	↑	[17]
Moisture variations	↓	(↓)	(↓)	[56]
Oxygen availability	↓	↓	↓	³⁾
Temperature	↓	↓	↓	³⁾

Legend

↑ (↓) indicates an increase (decrease) in threshold level with an increase of the concerning factor; — indicates no influence on the threshold value.

1) no results reported, 2) contradictory results reported in literature, 3) according to theoretical considerations

3 Definitions

3.1 Critical chloride content

The *critical chloride content* or *chloride threshold value* in concrete is usually defined as the chloride content required for depassivation of the steel (definition 1). However, depassivation of the reinforcement may not always lead to any deterioration: *e.g.* in very dry concrete the corrosion rates are kept low due to ohmic control of the current flow or in water-saturated the cathodic reaction is inhibited by low oxygen availability which limits the corrosion rate. Thus the critical chloride content can also be defined as the chloride content associated with visible or acceptable deterioration of the reinforced concrete structure (definition 2).

Fig. 4 illustrates these two different definitions by combining Tuutti's corrosion model [57] with an assumed constant chloride ingress leading to a linear increase in chloride concentration at the steel reinforcement. Different chloride thresholds are obtained by using different definitions.

It has to be noted that whereas in definition 1, the depassivation depends on the chloride concentration at the rebar, in definition 2 the higher critical chloride contents associated with an acceptable degree of corrosion is only the result of a longer time passing until the chloride concentration is determined. If, hypothetically, the chloride ingress would stop after depassivation, the chloride threshold according to definition 2 would not be higher. Moreover, in practice the corrosion rate is not constant during propagation. Also the term “acceptable degree” is somewhat imprecise and confusing.

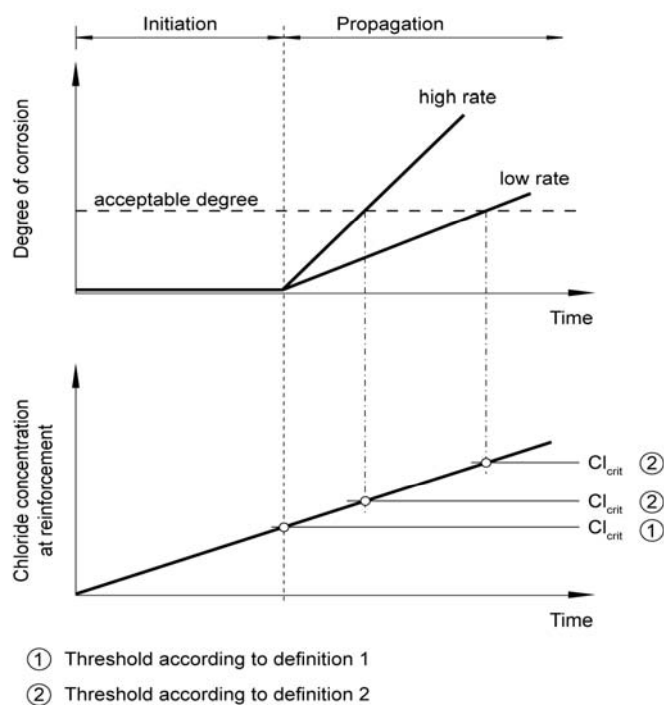


Fig. 4. Definitions for chloride thresholds (based on Tuutti's model [57])

3.2 Depassivation / Onset of corrosion

If the chloride concentration at the surface of the reinforcement reaches a certain threshold value, the protecting passive layer is destroyed locally and pitting corrosion can start, provided that enough moisture and oxygen is available at the steel surface. However, depassivation does not occur as an instant event; it is considered as a period of time during which the depassivation process takes place from the first defect until active corrosion is established [16].

It is thus important to define depassivation accurately, especially with regard to measurement techniques aimed at the detection of depassivation. It is of course impossible to detect the very start, *e.g.* the first local defect at the passive layer. A certain amount of corrosion is necessary in order to measure depassivation by potential measurements or by measuring the corrosion rate. From a practical view, it is also the corrosion that is of interest and not directly the breakdown of the passive layer.

In section 4.3 it will be dealt with several possible methods to detect depassivation and with what definition is used.

3.3 Expression of critical chloride content

The critical chloride content is most commonly expressed as *total chloride content relative to the weight of the cement*. The main reason for this is the fact that the determination of total chloride content in an existing structure is relatively simple and well documented in standards [58-60].

Since the determination of the binder content in hardened cement is inaccurate, it is sometimes preferred to express the chloride threshold level as *total chloride content relative to the weight of the concrete*.

As was pointed out previously, chloride can be present in concrete in the form of free and bound chlorides, whereas only the free chloride is considered to initiate pitting corrosion. Thus, chloride threshold values are also expressed by use of *free chloride contents*, either related to the weight of cement or to the weight of concrete.

The last form to express critical chloride thresholds relates the concentration of (free) chloride to the pH of the pore solution. Many authors have reported Cl^-/OH^- ratios as critical chloride content, mainly Hausmann [18] and Gouda [19] (see section 2.1), but also others [48,51,61-63]. It was shown that the Cl^-/OH^- ratio depends on the pH: The Cl^-/OH^- threshold ratio increases with higher pH, *i.e.* the inhibiting effect of OH^- ions is stronger at higher pH levels [51]. Thus, it is not sufficient to only consider the ratio of chloride ions and hydroxide ions as a critical threshold value; also the pH value must be taken into account.

The various forms to express chloride contents reflect both the destructive species (chloride) and the inhibitive properties of the concrete in different ways. The fact that only the chloride that is freely available in the pore solution is of importance with regard to corrosion initiation should favour the use of a free chloride content, either expressed by weight of cement/concrete or as Cl^-/OH^- ratio. However, also bound chloride presents a corrosion risk since it can be released as a consequence of various factors, among them a fall in pH [20,21]. Variations in pH may affect a structure globally, *e.g.* in case of carbonation, or locally, *e.g.* in macroscopic voids at the steel-concrete interface or in the vicinity of pits.

As was presented in section 2, a variety of factors affects the chloride content required to initiate corrosion. The alkalinity of the concrete is a main parameter in protecting the steel and thus chloride threshold levels have been expressed by relating the aggressive ion concentration to the concentration of OH^- ions in the pore solution. This was considered as the most accurate way to express critical chloride contents, but Glass and Buenfeld argue that this is not supported by analysis of available data in literature [13]. They analysed reported critical chloride threshold values and concluded that presenting critical chloride thresholds is best done in the form of total chloride by weight of cement. They mainly argue that the inhibitive properties of the concrete cannot be expressed only by the OH^- concentration in the pore solution. It is not only the pH, but also other factors such as the alkaline reserves of the concrete (buffer capacity) and the condition of the steel-concrete interface that determine the critical chloride content. Moreover, they point out that if only the free chloride is taken into account, the corrosion risk presented by bound chloride is ignored. Also, the span of reported threshold values is much bigger if they are expressed as free chloride instead of total chloride, which might be due to the non-linear relationship between bound and free chlorides, where a small range in the total chloride content corresponds to a larger range in free chloride. Variations resulting from other factors affecting the threshold level are thus amplified when presented as free chloride content [13].

From a practical point of view, it is important to bear also in mind that it is nearly impossible or at least very difficult to measure the free chloride content or the pH of the pore solution in an existing structure. It is comparatively simple to determine the total chloride and to relate it to the weight of concrete or cement (if the cement content is known or assumptions are made).

Table 3 sums up the main forms of expression of chloride contents in concrete and shows how they reflect the aggressive ion content and inhibitive properties of the concrete.

Table 3. Possibilities to express the critical chloride content

Aggressive species	Inhibitive property	expressed as...
Total chloride	by weight of cement/binder	% by weight
	by weight of concrete	% by weight
Free chloride	by weight of cement/binder	% by weight
	by weight of concrete	% by weight
Free chloride ion concentration	–	mole/l
	by OH ⁻ concentration	[Cl ⁻]/[OH ⁻] ratio

4 Testing methods

4.1 Methods for determining the total chloride content

The analysis of total chloride is frequently applied in practice and well documented in standards [58-60]. The total chloride content in concrete is usually determined by analysing cores drilled from hardened concrete, which are cut in slices of a certain thickness (*e.g.* 5 mm) in order to obtain a chloride profile. The sample is then crushed and powdered and dissolved in dilute nitric acid.

Dhir *et al.* [64] compared various methods to determine the total chloride content in concrete on OPC concrete specimens with mixed-in (and thus known) chloride. They found that the quantity of chloride extracted depends on the strength and dissolution time of the nitric acid; since different methods use different HNO₃ concentrations, the measured acid soluble chloride content varies accordingly. The results also suggested that the acid extraction technique cannot completely dissolve all the chlorides from the powder samples; the authors reported values in the range of 70...90% of the true content. They noted, however, that the chloride might be less easily extracted because mixed-in chloride was used, which is stronger bound to the cement paste.

A more expensive but very accurate way is to determine the total chloride content in concrete powder samples by X-ray fluorescence spectrometry (XRF) [64].

In a recent round robin test [65] methods for the analysis of total chloride were applied by 30 laboratories around the world and good a reproducibility was found for all of the methods. The highest reliability was given by the method that each laboratory currently used, which indicates that practice plays a major role in this kind of determination.

4.2 Methods for determining the free chloride content

4.2.1 Pore solution expression

The technique of expressing pore water from cement paste, mortar or concrete is well established and has been used by many researchers. A cylindrical sample is placed in the expression device and pressure is applied and kept constant for a certain time until a sufficient amount of pore solution is expressed. The collected pore solution is then ready for chemical analysis. Tritthart investigated the technique and concluded that the technique is applicable to determine the chloride concentration in pore solution with a good reproducibility [66].

It has been noted that under the pressure loosely bound chloride is released and increases the free chloride content in the expressed solution; this may result in an overestimation of the free chloride content [67]. The use of the pore press might also present difficulties when concrete with lower w/c ratios, coarse aggregate particles or rather dry specimens are investigated [68].

It has to be kept in mind that the pore solution expression technique results in an average value of the concrete volume under investigation; in case of high concentration gradients in the pore solution this may lead to inaccurate results.

4.2.2 Leaching techniques

Leaching techniques are based on mixing crushed or ground samples with a solvent and measuring the amount of chloride passing into solution. A variety of methods have been investigated using different solvents or different procedures with regard to leaching time and temperature.

As solvent usually distilled water is used. Alternatives such as methanol or ethyl alcohol have been investigated but both proved to be extremely ineffective at leaching out the free chloride; measured concentrations were in the range of 5...10% compared to the free chloride concentration obtained from pore solution expression [66,69].

The amount of chloride leached appears to depend on time during which the sample is in contact with the leaching media and on temperature. Arya *et al.* [69] investigated different extraction procedures, namely a) standing powdered samples in distilled water at 20° C for 48 h or 72 h, b) stirring the mixture at 20° C for 6 h and c) boiling the mixture for 5 min and standing for 55 min. The results were compared to pore solution expression (considered as true value). At chloride concentrations up to 1% by weight of cement (mixed-in) much higher chloride concentrations were measured compared to pore water expression, whereas in the range from 1.5 to 2% chloride by weight of cement the leached chloride concentration was lower than the true value. It was concluded that none of the investigated methods was sufficiently accurate over the range of chloride contents tested, but that the most accurate procedure can be selected if the total chloride content is known. In a later study [68] it was found that not only the total chloride content but also other parameters such as the cement type and source of chloride (mixed-in or external) have to be known in order to select an accurate leaching procedure and that thus the leaching technique is not practical for determining the free chloride content.

Recently, Castellote *et al.* [70] presented a leaching method based on an alkaline solvent to extract the free chloride. In the study, the authors tested the method on OPC mortar specimens with mixed-in NaCl and compared the results with the pore water expression technique. The procedure does not involve powdering of the concrete, but only splitting it into a sample weighing 3 g. The sample is then placed in the glass device and 2 ml of 0.3 M NaOH added. After stirring for 30 seconds the sample is left to rest in the solvent for 24 h and then the solution is analysed. At a total chloride content of 0.5% by weight of sample the leaching method overestimated the free chloride content rather remarkably (46% bias), but at higher chloride contents > 1% by weight of sample the proposed technique was in better accordance with pore water extraction. However, it has to be noted that rather high chloride contents have been investigated in this work and it is questionable if the technique is also accurate at lower and more practical concentrations.

The chloride concentrations obtained from leaching methods are often referred to as *water soluble chloride* (if water is the solvent) and sometimes considered to be equal to *free chloride*. These leaching techniques are rarely used in European practice. Contrary to Europe, water soluble chloride analysis is a standard method used in North America [71]: In the “Soxhlet extraction technique” boiling water is used to extract chloride from concrete chips.

4.2.3 Chloride sensors

The free chloride content in the pore solution can also be measured by use of ion selective electrodes embedded in the concrete. The interfacial potential of a silver/silver chloride follows Nernst's law and depends on the activity chloride ions in the solution.

Atkins *et al.* [72] first tested the application of Ag/AgCl electrodes to measure the free chloride concentration in simulated pore solution and in cement paste. The results showed good correlation between measured concentration in extracted pore solution and values derived from potential readings at the Ag/AgCl electrodes.

Elsener *et al.* [73-75] investigated the accuracy and long term stability of Ag/AgCl electrodes in synthetic pore solution and in mortar specimens. Excellent stability and reproducibility was found during the investigated time span of more than 550 days. Lots of chloride sensors have been embedded also in monitoring projects on concrete structures and no failures were reported [76].

4.3 Methods for determining the depassivation process

4.3.1 Measurement of the corrosion rate

Close to the corrosion potential the polarisation curve is linear. By measuring the polarisation curve experimentally in a small range around the equilibrium potential, the slope $\Delta E/\Delta I$ of the curve can be obtained. This slope is defined as *polarisation resistance* R_p , which is related to the corrosion current by the *Stern-Geary-equation*:

$$i_{corr} = \frac{b_{ox} \cdot b_{red}}{b_{ox} + b_{red}} \cdot \frac{1}{R_p} \quad (2)$$

This equation is often expressed in a simplified way as:

$$i_{corr} = \frac{B}{R_p} \quad (3)$$

In this form, B is a constant containing the Tafel slopes of both the oxidation and reduction reactions and usually $B = 26$ mV in the case of actively corroding steel in concrete [77].

With this technique, referred to as linear polarisation resistance measurement (LPR), it is thus possible to determine the instantaneous corrosion rate. In order to detect depassivation, a significant corrosion rate has to be defined. In a concrete which contains substantial moisture and oxygen, significant corrosion is characterized by an averaged sustained corrosion rate higher than $0.1 \dots 0.2 \mu\text{A}/\text{cm}^2$ [16]. The reasons for this value are a) the empirical observation that the measured corrosion current in solution and mortar studies was never below $0.1 \mu\text{A}/\text{cm}^2$ when rust was observed and b) that $1.16 \mu\text{m}/\text{year}$ of formation of rust may lead to cracking within $5 \dots 10$ years [78]. This definition of depassivation above a current density of $0.1 \mu\text{A}/\text{cm}^2$ is generally accepted [77].

It has to be noted that the measured corrosion rate is an average value over the exposed steel area. The local current density inside the pit is typically very high.

4.3.2 Other methods

Potential shift. Since actively corroding steel has a much more negative potential than passive steel in concrete it is also possible to detect depassivation based on potential readings. In this case a certain shift in corrosion potential indicates depassivation. This shift is usually very pronounced and many researchers used this as criterion in order to identify the time of depassivation [15,18,19]. However, it has to be kept in mind that a shift in potential can have several reasons and does not always mean significant activity.

Macro cell current. If the steel electrode of interest is connected with another steel electrode (*e.g.* counter electrode, external stainless steel, etc) the macro cell current between those two electrodes can be monitored. An increase indicates depassivation. In some cases the working electrode is polarised and held constant at a certain potential during the experiments (potentiostatic control); the current is monitored in order to detect depassivation.

Electrochemical impedance spectroscopy (EIS). EIS is performed by imposing an external sinusoidal voltage signal with low amplitude and varying frequency to the system. The current response is measured. Electrochemical impedance spectra can be interpreted by use of an equivalent electrical circuit consisting of resistances and capacitors; by this, values such as the polarisation resistance can be obtained in order to calculate the corrosion rate by application of eq. (3) [51,79].

Weight loss. The steel weight loss of reinforcement can be determined by measuring the weight of corroding steel bars removed from concrete. In order to determine the remaining steel mass the bars have to be cleaned after removing from the concrete which may possibly result in some additional weight loss. This can be taken into account by determining the weight loss due to the cleaning procedure on separate steel bars [38].

Visual inspection. If the concrete is broken up and the steel exposed visual inspection of the steel surface can also be used to identify depassivation with the appearance of rust on the steel surface. As this is a destructive method it only can be performed once. Accordingly, the accuracy is very low, since it is not possible to know how much time has passed between depassivation and visual observation of rust. Moreover, the appearance of rust spots may take some time and, once present, does not necessarily mean significant and sustained corrosion activity. Visual inspection to detect depassivation has mostly been used in early work on corrosion initiation [4], but is sometimes also applied at present in addition to other techniques [14].

4.4 Laboratory methods for determining the critical chloride content

In order to experimentally find a certain chloride content at which corrosion starts the research has to include the following (Fig. 5):

- A steel electrode of interest embedded in a cement based material (cement paste, mortar, concrete) or immersed in a solution that simulates the concrete (synthetic pore solution, alkaline solution).
- Chloride present at the steel surface (admixed from the beginning, introduced to the hardened material later by some kind of exposure or by raising the concentration in the solution with time).
- Detection of the time of depassivation, *e.g.* by measuring the corrosion current, steel potential, weight loss, visual inspection, etc (see section 4.3).

- Quantifying the chloride content (total or free chloride or Cl^-/OH^- ratio) at the time of depassivation by a technique such as those described in sections 4.1 and 4.2.

These various possibilities to simulate the system “reinforcing steel in concrete” (a) and the chloride ingress (b), as well as the measurement and detection techniques (c–d) offer a lot of possible combinations to perform laboratory studies (Fig. 5).

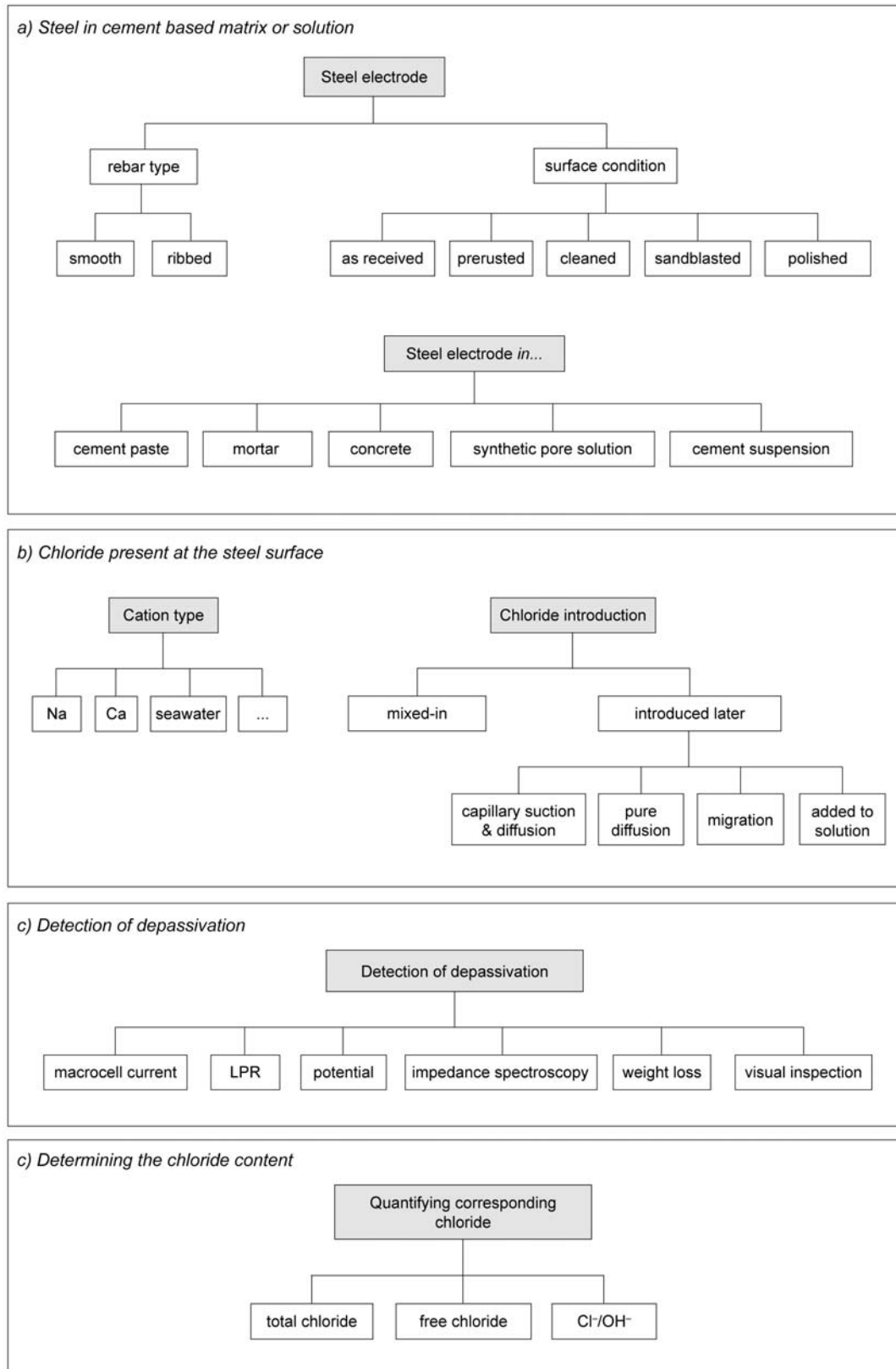


Fig. 5. Possibilities to study critical chloride content

Numerous investigations have been undertaken and a wide range of critical chloride contents have been reported, not least as a result of very different experimental procedures. In addition, also several proposals have been made for laboratory methods in order to determine the chloride threshold. A few examples are presented here:

- Alonso *et al.* (2002) [16,23] proposed a potentiostatic method based on small mortar specimens of 2 x 2 x 8 cm size with an embedded steel bar and a cover thickness of 5 mm. After curing (7 days at 95% RH and 20° C) the free corrosion potential and the corrosion rate (LPR) of the steel bar are measured. Subsequently, the specimens are immersed in a 0.5 M NaCl solution and the steel bars are polarized by an external counter electrode and maintained at a constant potential. Various potentials from +250 to –650 mV SCE are investigated on different samples. The current required for the polarisation is monitored in order to detect depassivation; as soon as an increase of the current is noticed the specimen is removed from the testing arrangement and polarisation is stopped. After a waiting time of 1 h the free corrosion potential and corrosion current are measured. Finally, the specimen is crushed and the steel surface is visually inspected. Also chloride analysis is performed on mortar samples at the level of the rebar; the total chloride content was determined using X-ray fluorescence and the free chloride content is determined by a leaching method. Similarly, also the OH[–] content is determined. With this method it is possible to study the relationship between potential and chloride threshold.
- Trejo and Pillai (2003) [80] presented a methodology for evaluating the critical chloride content of steel in mortar specimens. Specimens are cast with an embedded steel as working electrode and a nichrome mesh at the same depth. In addition, a reference electrode is embedded in a Luggin probe whereas the tip of the probe is placed within 2 mm of the steel reinforcement surface. A reservoir containing a 3.5% chloride ion solution and a cathode (nichrome mesh) are placed on top of the specimen. By applying an electric field between the outer (cathode) and inner nichrome mesh (anode), chloride ions are drawn towards the reinforcement steel. A voltage of 20 V is applied for 12 h per day during 4 or 5 days. Then, the samples are allowed to rest for 42 h, followed by LPR measurements of the embedded steel. If no depassivation is detected, the specimens are subjected to the migration process again for 6 h, followed by a 42 h rest period and LPR measurements. This will continue until a significant corrosion current is measured. Then, chloride analysis at the steel-mortar interface is carried on ground mortar (total chloride analysis). This yields the critical chloride content for the concerning steel and mortar.

In this setup, the anode for the migration process is close to the reinforcement steel (WE). In the electric field OH[–] ions move towards the anode and there oxidize as follows:



The pH of the pore solution in the region of the anode and of the steel will thus fall with migration time. It was found that the pH fell from initially 13.1 to 12.4 after 8 days; certainly, this affects the onset of corrosion.

- Nygaard and Geiker (2005) [81] proposed a method for measuring the chloride threshold level in concrete. They used OPC concrete specimens (w/c = 0.45,

aggregates 0–16 mm) with six embedded smooth reinforcement bars (diameter 10 mm). After casting and curing the concrete cover was cut and reduced to 5, 10, 15, 20 and 25 mm. The samples were then dried at 22% RH and 30° C for 60 days and subsequently immersed in a saline solution. Due to capillary action, chloride bearing water penetrated the concrete cover and thus the chloride content at the rebars increased. The corrosion activity of the steel bars was monitored by potentiostatic control, *i.e.* the steel electrodes were maintained at a potential of 0 mV SCE and the current required was measured until a significant increase indicated depassivation. The section with the concerning steel was then removed by cutting and the remaining specimen was put back into the solution. The removed part was split along the rebar allowing visual examination of the steel surface. The total chloride content was determined on powder samples ground at the cut concrete surface (depth of reinforcement) and yielded the critical chloride content for the concerning corrosion cell.

4.5 Examination of existing structures (field method)

Vennesland [82] proposed a procedure for field determination of critical chloride content. Areas where the reinforcement is depassivated and actively corroding are detected by potential mapping and/or corrosion rate measurements. In areas where no corrosion damage is visible two locations above reinforcing steel are selected: one location with the highest probability and one location with the lowest probability for active corrosion. Total chloride analysis is performed on concrete samples collected at the depth of the reinforcement either from drilled cores or from samples chiseled in the field. The critical chloride content is equal to the chloride content at the depth of the reinforcement and is expressed as total chloride relative to weight of dry concrete.

5 Literature evaluation

A variety of investigations dealing with chloride threshold values has been undertaken and published in literature. The wide range of reported critical chloride contents is not only due to the complexity of the situation itself (influencing factors, section 2), but also a result of various definitions and measurement techniques used (sections 3 and 4). As has been pointed out in section 4.4 the issue of critical chloride content can be approached by a lot of possible procedures.

In the following sections, available publications are briefly summarized and compared with regard to the materials used, the manner of chloride introduction, the measurement techniques and the reported threshold values. Only studies are considered which included all of the points a) – d) mentioned in section 4.4 (Fig. 5). Some studies also reported critical chloride contents as a result of examination of the pore solution and by calculating the critical chloride content based on assumptions, *e.g.* a certain Cl^-/OH^- ratio such as the common one of 0.6 according to Hausmann [18]. Since no depassivation detection was included in these studies, they do not offer new findings with regard to chloride threshold values. These publications are briefly mentioned in a separate section. Table 4 and 5 summarise the results of the evaluated references.

5.1 Reported chloride threshold values

5.1.1 Reported values based on laboratory corrosion investigations

Hausmann [18] performed corrosion experiments with steel bars immersed in alkaline solutions and different chloride concentrations. As solution mainly saturated calcium hydroxide was used. The solutions were aerated with bubbles of oxygen at the steel surface. The potentials of the steel were measured and indicated the onset of corrosion. Due to the improved corrosion resistance with increased alkalinity Hausmann suggested to present chloride threshold values as Cl^-/OH^- ratios. He reported values in the range of 0.50 to 1.08 (with oxygen present at the steel) and from probabilistic considerations he proposed a threshold ratio of 0.6. It was also shown, that in the absence of oxygen, much higher chloride concentrations are tolerable.

In a study published in 1969, Richartz [4] mainly dealt with chloride binding properties of cement, but also performed some corrosion experiments. Smooth steel bars had been embedded in OPC mortar specimens ($w/c = 0.45$) that contained chloride from 0.04% to 0.40% by weight of cement, added as calcium chloride in the mix. After casting and curing, the specimens were stored at 20 °C and 65% RH and were periodically wetted with distilled water. Visual inspection after up to three years did not reveal any rust on the steel surface. This was in accordance with his findings concerning the binding capacity of cement, which were that during hydration of cement up to 0.4% chloride can be bound. It was also from this work, that the common criterion of a critical chloride content equal to 0.4% by weight of cement was derived.

Gouda [19] studied the behaviour of reinforcing steel in different alkaline solutions in presence of sodium chloride. Prior to immersion the steel was polished, degreased and stored in acid. The steel potential was measured during anodic polarisation and a relationship between the pH of the solution and the chloride concentration that can be tolerated was found in the form of eq. (1) presented in section 2.1.

Gouda and Halaka [46] investigated the performance of steel bars embedded in concrete (mix proportions as cement : sand : gravel : water = 1 : 2.3 : 3.4 : 0.6) and immersed in mortar suspension. OPC and cement containing 35% GGBS was used for both the concrete ($w/c = 0.6$) and the suspension. The mortar suspension was produced by casting mortar specimens, which were ground after curing and mixed with water. Chloride was introduced by using different mixing waters such as tap water, mineral water and sea water. The steel was anodically polarised and the potential measured vs. time. The reported tolerable chloride content was 0.45% chloride by weight of sample for the OPC concrete and 0.15% chloride by weight of sample for the slag containing concrete. For the steel immersed in mortar suspension threshold values were found as 0.61% chloride by weight of sample (OPC) and 0.3% chloride by weight of sample (GGBS).

In 1975, Stratfull *et al.* [83] reported the results of the inspection of twenty-two bridges, that mainly had been exposed to de-icing salts. The steel was considered to be passive as long as the potentials were higher than -350 mV CSE (on site potential measurements). Chloride analysis was performed on cores drilled from the structures. The authors found that the amount of chloride in the concrete associated with the incidence of active corrosion was about 0.59 kg/m^3 . In one bridge, a maximum chloride content of 4.7 kg/m^3 was found without any corrosion. By assumption of a concrete density of $2'300 \text{ kg/m}^3$ and cement contents of 350 kg/m^3 the reported results can be transformed to chloride percentages by weight of cement; this yields 0.2...1.4%.

Locke and Siman [84] measured the corrosion rate of reinforcing steel in salt-contaminated OPC concrete. Reinforcing steel bars “as received” were cleaned with

acetone and cast in concrete cylinders containing various levels of admixed sodium chloride (0...1% NaCl per weight of concrete). The specimens were cured 28 days in a water cabinet and then stored under laboratory exposure conditions for about one month. The corrosion rate was then determined by LPR measurements. For chloride additions up to 0.1% NaCl per weight of concrete the corrosion rates were almost identical; a significant increase occurred by changing the chloride content from 0.1 to 0.2% NaCl by weight of concrete. This equals to a critical chloride content of 0.4...0.8% chloride by weight of cement.

Elsener and Böhni [79] performed AC-impedance measurements on mild steel rods embedded in OPC mortar. Cylindrical mortar specimens ($w/c = 0.5$) containing a centrally placed steel bar were cast with a cover depth of 7 mm (with calcium chloride added to the mix) and cured for 28 days at 100% RH. One series of experiments was then carried out under full immersion in chloride containing, saturated calcium hydroxide solutions; the other series was first kept at 100% RH during 12 weeks and then at 60% RH. For the impedance measurements, the specimens were put into solutions open to air. The borderline between pitting corrosion and passive behaviour was found at a chloride content of $0.25 < \text{critical chloride content} < 0.5\%$ chloride by weight of cement.

Hope and Ip [85] examined OPC concrete slabs ($w/c = 0.45$) with embedded steel rods (polished prior to casting). One series contained admixed calcium chloride dihydrate and another series was produced with chloride bearing aggregates. After curing for 14 days, one half of the slabs from each series was stored outdoors and the remaining slabs were subjected to wet/dry cycles (3 days in aerated water / 11 days drying in the laboratory). Resistivity, LPR, AC-impedance and potential measurements were conducted periodically. Also, after certain periods the steel rods were visually inspected and the weight loss was determined gravimetrically. The chloride threshold values reported were similar for both indoor and outdoor samples and are in the range of 0.096...0.193% chloride by weight of cement.

Yonezawa *et al.* [25] investigated the influence of the steel-concrete interface on the corrosion behaviour. Steel bars (diameter 8 mm) were polished and then embedded in small OPC mortar specimens ($w/c = 0.5$) with a cover depth of only 7...11.6 mm. After demoulding, the samples were immersed in saturated $\text{Ca}(\text{OH})_2$ for two weeks and then immersed in alkaline chloride containing solutions. For some samples, chloride was directly added to the mix. In order to investigate the influence of the steel-mortar interface the steel surface was separated from the mortar by a filter paper in some specimens. Also, some steel electrodes were not embedded in mortar but only immersed in alkaline solutions. The steel potential and the linear polarisation resistance were measured during immersion and indicated depassivation. The steel-mortar interface of split specimens was examined by SEM and X-ray analysis and chloride and hydroxyl ion concentrations were analyzed on pore water expressed from parallel samples. It was found that the condition of the steel-mortar interface is important for corrosion initiation: Threshold Cl^-/OH^- ratios in the range of 7...45 were reported for the specimens with "normal" interface conditions, whereas those manipulated by the presence of a filter paper only Cl^-/OH^- ratios in the range of 7...22. The passivity of steel in mortar is sustained at much higher Cl^-/OH^- ratios than in case of steel electrodes immersed directly in alkaline solutions, where the reported Cl^-/OH^- threshold was only 5.

Goñi and Andrade [61] measured the potential and corrosion rate of steel bars immersed in synthetic concrete pore solutions with different additions of NaCl and CaCl_2 . The steel bars were mechanically polished and degreased in acetone before the investigation. From the measured corrosion rates, mean values were calculated over time. A linear relationship between the logarithm of I_{corr} and the logarithm of the Cl^-/OH^- ratio was found. Active

corrosion, identified by a corrosion rate higher than $0.1 \dots 0.2 \mu\text{A}/\text{cm}^2$, was reported for Cl^-/OH^- ratios in the range of $0.25 \dots 0.8$.

Hansson and Sørensen [27] evaluated the effect of various parameters on critical chloride content. Mortar prisms with a centrally placed, smooth and cleaned carbon steel rod were prepared with different cement types: OPC, sulphate resistant Portland cement (SRPC), rapid hardening Portland cement (RHPC; 3% FA), fly ash cement (22% FA) and Portland cement with addition of 10% microsilica. Also, various curing times (3, 7, 14 and 31 days at 100% RH) and w/c ratios from 0.4 to 0.6 were tested. Chloride was introduced 30 days after casting by immersion in an alkaline sodium or calcium chloride solution. The steel rods were held at a constant potential of 0 mV SCE and the current flowing between the embedded steel and an external stainless steel bar was recorded until it increased by several orders of magnitude (initiation of corrosion). At this time, some samples were analyzed for chloride content and the remaining samples were put vertically in the chloride solution so that a large part of their surfaces was exposed to air. From this point, the polarisation was stopped and the free corrosion potential and corrosion rate were monitored. Thus, the specimens were submerged until corrosion was initiated and then exposed to air in order to measure the corrosion rate in the presence of oxygen. The reported chloride threshold values were 0.4% chloride by weight of cement (SF), 0.85% chloride by weight of cement (SRPC) and $0.56 \dots 1.37\%$ chloride by weight of cement for the different OPC mixes. Since these values are relatively high in comparison with practical measurements additional samples with ribbed steel bars (sandblasted, as received, rusted) were made, but no according critical chloride contents were reported. Schiessl and Raupach [86] measured the macro cell current between steel electrodes embedded in different concrete areas. Chloride was either added to the mix or introduced later by capillary suction or diffusion. Various types of cement such as OPC and blended cements containing FA, SF or GGBS as well as different w/c ratios from 0.4 to 0.6 were investigated. Critical chloride contents were found in the range of $0.5 \dots 2.0\%$ by weight of cement.

Lambert *et al.* [62] and Page *et al.* [63] investigated steel rods embedded in cement paste and concrete with both internal chlorides added in the mix and external chlorides that were introduced by casting a pond (5% sodium chloride solution) on the upper surface of the hardened slabs. Different methods for the introduction of external chloride were utilized: a) constant exposure to the NaCl solution, b) weekly wet/dry cycle and c) monthly wet/dry cycle. Ordinary Portland cement (OPC) and sulphate resistant Portland cement (SRPC) and two different aggregates – quartzite and limestone – were used. Prior to embedment the steel rods were degreased with acetone. The potential and the corrosion rate were measured during two years. Passivity, characterized by corrosion rates below $0.1 \mu\text{A}/\text{cm}^2$, was maintained until a threshold ratio Cl^-/OH^- of approximately 3 was exceeded, but also values up to 20 were recorded without significant corrosion. Expressed in the form of total chloride this was 1.5% by weight of cement.

Thomas *et al.* [38,87] evaluated the effect of fly ash on chloride threshold values. Concrete specimens with different types of FA containing cements (0%, 15%, 30%, 50%) were cast with four embedded mild steel bars (ribbed). After curing, the samples were placed in a tidal zone (marine exposure). Chloride analysis and weight loss of the steel bars were measured after 1, 2 and 4 years of exposure. Reported chloride threshold values are 0.70% chloride by weight of cement for the OPC concrete and then decreasing with increasing FA content: 0.65% (15% FA), 0.50% (30% FA) and 0.20% by weight of cement (50% FA).

Pettersson [88] investigated the influence of various parameters such as the cement type and water/binder ratio on the critical chloride content. Mortar specimens with w/b ratios

0.4, 0.5 and 0.6 were produced using OPC and OPC with addition of FA or SF. Steel bars were cleaned with acetone prior to casting. The specimens were cured at 100% RH for 14 days and subsequently at 50% RH for another 14 days. After curing some of the samples were immersed in a 1 M NaCl solution and some were exposed to a weekly spraying procedure with salt containing water. The corrosion rates were monitored by periodical LPR measurements. After depassivation of the steel, mortar samples were taken from the interfacial zone for total chloride analysis. It was also tried to extract pore solution, but this appeared to be difficult in some cases. The free chloride content was then calculated by use of bound-free-relationships published by Tuutti and Byfors. It was found that the w/b ratio influences the time required for the chloride to reach the steel surface and the amount of water available in the concrete. At a higher w/b ratio, the free chloride was thus more diluted due to a higher amount of water. In comparison with the OPC samples, lower chloride thresholds were found for SF containing cement (perhaps due to a lower pH) and higher thresholds were reported for FA containing cements (perhaps due to a high pH and reduced oxygen supply). Some additional specimens were prepared with mixed-in chloride, but no significant difference was found regarding the critical chloride content. The time of initiation, however, was shorter in this case.

Pettersson [35] measured the free chloride and hydroxyl ion concentration in mortar and concrete specimens that contained admixed chloride or chloride penetrated due to spraying with a saturated sodium chloride solution. Ribbed steel bars were embedded in mortar (w/c = 0.3...0.75) and concrete (w/c = 0.5...0.75) specimens and monitored by LPR measurements. The samples were cured at different laboratory conditions (80%, 60% and 50% RH at 20 °C) or outdoors. One set contained also silica fume. When depassivation was detected concrete near the steel surface was removed and analysed for chloride and hydroxyl content (by leaching with distilled water). In the case of the mortar specimens, pore solution was expressed at the depth of the rebars and analysed. It was shown that the critical chloride content strongly depends on the w/c ratio and decreased from 6, expressed as Cl^-/OH^- ratio, for w/c = 0.3...0.4 to 2.5 for w/c = 0.75. The chloride threshold was found to be lower for SF containing specimens in comparison to OPC specimens.

Mammoliti *et al.* [50] investigated the influence of the surface finish of steel electrodes immersed in alkaline solutions on pitting corrosion. Different steel electrodes were used such as ordinary ribbed steel bars (degreased in acetone) and steel surfaces ground and/or polished to different finishes. The samples were tested in saturated calcium hydroxide solution of pH 12.5 and simulated pore solution of pH 13.3 containing NaOH and KOH by anodic polarisation. For some tests, the saturated calcium hydroxide solution was filtered and also contained 0.1 % $\text{Ca}(\text{NO}_2)$ as a corrosion inhibitor. In this solution, pitting was initiated at 0.5% chloride (0.14 mole/l) in the ground samples and at 1% chloride (0.28 mole/l) in the ribbed (degreased) samples. In the case of the polished specimens, corrosion started at 1.5% chloride (0.42 mole/l). In the more alkaline electrolyte (pH 13.3) none of the samples exhibited any consistent corrosion even at high chloride contents.

Schiessl and Breit [47] studied the corrosion behaviour of steel in concrete after local patch repair. Specimens were cast with different areas of concrete simulating undamaged and chloride containing concrete. Chloride was either added directly to the mixing water or introduced later by external chloride exposure. Pieces of reinforcement steel were embedded in the different concrete areas and connected in order to monitor the macro cell currents. Concrete produced with OPC, GGBS and FA containing cements were studied; the w/c ratio varied from 0.5 to 0.7. The critical chloride content reported was 0.5...1.0% chloride by weight of cement for the OPC and 1.0...1.5% by weight of cement for GGBS and FA containing cements.

Elsener *et al.* [75] measured the free chloride concentration with help of embedded Ag/AgCl electrodes in OPC mortar blocks during immersion in a sodium chloride containing solution. The potential of steel bars, embedded at different depths, was also monitored and indicated depassivation. The reported free chloride concentration necessary for onset of corrosion was in the range of 0.44...0.65 mole/l.

Breit [11] investigated the corrosion behaviour of steel bars immersed in alkaline solutions at different pH levels between 12 and 14. After cleaning the steel bars in acetone they were immersed in the alkaline and at that time chloride free solutions and left to rest for 48 hours in order to reach initial passivation. Sodium chloride was then added to the solution and the working electrodes were anodically polarised in steps of 0.05 V per 12 h (starting from the reached corrosion potential). The current was monitored until it indicated depassivation. At a pH of 13.5 a critical chloride content of 0.056 mol/l or a corresponding ratio Cl^-/OH^- of 0.26 was reported. Also, a linear log-log-relationship between the tolerable chloride content and the concentration of inhibiting OH^- ions similar to the one presented by Gouda [19] was found; the corrosion-inducing Cl^-/OH^- ratio falls with decreasing pH and is not a constant value as *e.g.* the criterion of 0.6 proposed by Hausmann [18].

Breit [89] also conducted experiments with mortar specimens immersed in alkaline, sodium chloride bearing solutions. Eleven different mortar mixes ($w/c = 0.5 \dots 0.6$) were investigated using OPC, blast furnace slag cement (GGBS), high-sulphate resistant Portland cement (SRPC) and OPC with addition of silica fume (SF) and fly ash (FA). In the cylindrical specimens a smooth steel bar was embedded in mortar with a cover depth of 7.5 mm. After curing in an alkaline solution, the specimens were immersed in sodium chloride solution. In one series, the working electrode was connected to an external mesh and the electric current was measured against time (without polarisation). In another series, a potential was applied between the mesh and the steel bar in order to polarize the steel constantly to +0.5 V versus the standard hydrogen electrode (SHE). As soon as depassivation was detected (by monitoring the electric current), chloride analysis was performed on drilled dust and the steel surface was visually examined. No corrosion was observed below 0.25% total chloride by mass of cement (lower limit) and the threshold values scattered up to 0.75% total chloride by mass of cement. In case of the SF containing cement a much smaller scatter was observed (0.25...0.40% by weight of cement).

Sandberg [90] studied the influence of several factors on critical chloride content. Large reinforced concrete slabs (100 cm x 70 cm x 10 cm) were produced and exposed to marine environment for several years. Ordinary ribbed steel bars were used as received from the supplier with concrete covers in the range of 10 to 20 mm. Various cement types were tested such as SRPC with and without addition of SF and FA as well as slag cement; the water/cement ratio varied from 0.30 to 0.75. The slabs were mounted on a floating pontoon and exposed to sea water, whereas the bottom part was submerged and the upper part was exposed to air. Depassivation was detected by monitoring of the steel potential and verified by LPR measurements or observing galvanostatic pulse response. Chloride analysis was performed after 7, 12, 24 and 60 months on drilled cores. Chloride threshold values were reported from 0.4 to 1.5% total chloride by weight of binder. Also corrosion cells consisting of 20 U-shaped smooth steel electrodes embedded in a concrete slab were exposed to seawater. Following the procedure by Yonezawa [25] defects at the steel-concrete interface were produced by applying filter paper to selected steel electrodes. Different w/c ratios from 0.4 to 0.5 and cement types (SRPC, SF, GGBS) were investigated. Besides exposure to seawater some specimens were also subjected to laboratory wetting and drying cycles. Chloride threshold values were found in a large

range starting at 0.2% total chloride per weight of binder up to values higher than 2.2%. It was shown that the artificially created defects at the steel-concrete interface had a strong negative effect on the critical chloride content.

Alonso *et al.* [14] studied chloride threshold values in OPC mortar specimens ($w/c = 0.5$). Ribbed and smooth steel bars were embedded in mortar containing admixed chlorides (in most cases sodium chloride, in one calcium chloride). After casting and demoulding the mortar specimens were kept at 100% RH and the steel potential, electric resistance and LPR were measured periodically. Chloride analysis was performed on broken specimens for total chloride (X-ray fluorescence) and free chloride (liquid extraction technique according to ref. [70]). At the end of the experiments, the steel bars were visually examined. A slightly higher corrosion activity for the ribbed steel in comparison with the smooth steel was found. Critical chloride contents were expressed in the form of total chloride (1.24...3.08 % by weight of cement), free chloride (0.39...1.16 % by weight of cement) and Cl^-/OH^- ratios (1.17...3.98).

Zimmermann *et al.* [15,91] investigated the corrosion initiation of mild steel bars in alkaline solutions, mortar specimens and on a real concrete structure. The solution experiments were performed in synthetic pore solutions with a pH of 13.4 with continuous oxygen supply and increasing chloride concentrations. The rebars were sandblasted and cleaned in ethanol prior to testing. The mortar blocks were prepared from OPC with a w/c ratio of 0.6 and contained five rebars (cover depth = 30 mm) and four chloride sensors in order to measure the free chloride concentration in the pore solution. After curing (28 days) and drying (10 days, 50°C) the mortar blocks were put in sodium chloride solution (3 mm immersion). Depassivation was detected by potential measurements and macro cell current readings. In the solution experiments, no corrosion was detected for Cl^-/OH^- ratios below 0.7, whereas at values higher than 1.7 the probability for corrosion was 100%. For the mortar specimens and also from experience with the real concrete structure, no corrosion was detected below a total chloride content of 0.25% by weight of cement or 0.045 mole/l free chloride in the pore solution; for a pitting corrosion probability of 90%, the threshold value reported was 1.25% total chloride by cement weight or 0.55 mole/l free chloride.

Li and Sagüés [51] tested the corrosion behaviour of different steel surface conditions in alkaline and chloride containing solutions. Mill scaled (as received), sandblasted and prerusted steel rebars were immersed in different alkaline solutions which were initially free of chloride. The chloride concentration was then increased in several steps and the corrosion potential was monitored. Periodically, also electrochemical impedance spectroscopy tests (EIS) were performed on selected specimens. It was found that the threshold ratio Cl^-/OH^- increased significantly with pH. All steel samples showed very low threshold Cl^-/OH^- ratios around 0.01...0.04 in the solution with pH 12.6, whereas at pH 13.6 threshold ratios in the range of 1...1.5 were found for the mill scaled and prerusted samples and 2...2.5 for the sandblasted samples.

Alonso *et al.* [23] investigated the relation between the steel potential and the critical chloride content and proposed a laboratory method for determining the critical chloride content (see section 4.4). Six different cement types were analyzed and the mortar mix had a w/c ratio of 0.5. For potentials more noble than -200 ± 50 mV SCE mean threshold values were 0.73% total chloride by weight of cement or 1.76 expressed as Cl^-/OH^- ratio. For potentials more negative than -200 ± 50 mV SCE a continuous increase in critical chloride content was noticed; reported values range from 0.5 to 8.34% total chloride by weight of cement or 1.7...20 if expressed as Cl^-/OH^- ratio.

Castellote *et al.* [92] determined the critical chloride content on mortar specimens that contained chloride introduced by migration. Three cubic mortar specimens ($w/c = 0.37$)

with an embedded steel bar (cover depth 35 mm) were cast from sulphate resistant Portland cement (CEM IV-B-32.5). A reservoir containing NaCl solution with a stainless steel inside was placed on top of the specimen and a steel plate was connected to the concrete at the bottom by use of a wet sponge. By this, an electric field was applied to the specimen and chloride ions migrated into the mortar. The steel potential was continuously monitored and periodically, also LPR measurements were conducted. At the time of depassivation, the specimen was split and total and free chloride analyses, as well as pore solution pH measurements were carried out. During the migration procedure, embedded Ag/AgCl electrodes allowed to follow the ingress of chloride qualitatively (no free chloride concentrations were calculated from the potential readings). A parallel specimen was studied without electrical acceleration, but only diffusion as the mechanism in order to move chloride into the mortar. Despite some influences and modifications introduced by the electric field, very similar results were obtained for the accelerated (migration) and natural (diffusion) tests (Table 4).

Trejo and Pillai [80] proposed a laboratory method for determining the critical chloride content on mortar specimens (see section 4.4). The reported chloride threshold values were in the range of 0.02...0.24% by weight of cement. The authors also calculated Cl^-/OH^- ratios which were in the range of 0.05...0.62. However, it is not clear from the information given in the publication how the free chloride was determined; only analysis for total chloride is mentioned.

Oh *et al.* [93] examined the threshold chloride concentration in concrete specimens. As test variables several types of cement were investigated: OPC, SRPC and cement containing FA (15% and 30%) or GGBS (30%). Concrete prisms were cast with a centrally embedded 13 mm steel bar. Half-cell potential measurements were performed every 3 days and after 30 days, the pore solution was extracted from the concrete around the rebar in order to determine chloride and hydroxide ion concentrations. The chloride binding capacity of SRPC was found to be lower than that of OPC. Also, a lower total chloride threshold value (0.45% by weight of binder) was reported for SRPC in comparison with OPC and FA or GGBS containing cements (0.68...0.97% by weight of binder).

Nygaard and Geiker [81] reported critical chloride contents in the range of 0.52...0.74% by mass of cement for OPC concrete (compare section 4.4).

Mohammed and Hamada [49] investigated steel bars with various surface conditions such as mill-scaled, polished, brown- and black-rusted and steel bars that were covered with a cement paste (pre-passivated) before casting. The steel bars were embedded in OPC concrete specimens that were submerged in seawater at 60 °C for 3.5 days and air dried for 3.5 days (30 cycles). Various electrochemical measurements, such as potential and LPR measurements were conducted to monitor the corrosion behaviour; passivity was defined as corrosion rates below $0.1 \mu A/cm^2$. Only water-soluble chlorides were determined in this study and corresponding threshold values, presented as water-soluble chloride by weight of cement, were reported as follows: polished steel (0.8%) > brown-rusted steel (0.5%) > mill-scaled steel (0.4%). For the pre-passivated and black-rusted steels, no threshold values were reported, but these are expected to be much higher.

Manera *et al.* [36] studied the influence of silica fume on critical chloride content in concrete. Cylindrical concrete specimens (aggregate 0–8 mm, w/c = 0.6) of 200 mm height and 60 mm diameter were cast. One mix was prepared using OPC and the other contained 10% SF. Steel bars were embedded in the specimens in the form of ribbed and smooth bars; also the effect of the steel surface was studied by sandblasting half of the steel bars of each type and using the other half as received. All the bars were immersed in saturated calcium hydroxide for 15 days prior the casting. The concrete specimens were

sealed and left for curing during 28 days and subsequently stored at laboratory environment (20 °C and 50% RH). After this, the electrochemical potential, the linear polarisation resistance and the concrete resistivity were measured. Critical chloride contents were found between 1.1 and 2.0% chloride by weight of cement in the case of OPC cement and between 0.6 and 1.2% by weight of cement in the case of SF containing cement. The difference in chloride threshold between the as received and sandblasted bars was found to be more evident than the difference between smooth and ribbed bars. Sandblasting appeared to elevate the chloride threshold level.

5.1.2 Reported values based on calculations

Studies that reported threshold values based only on assuming a certain Cl^-/OH^- ratio and then calculate a certain (free) chloride content:

Diamond [94] examined the pore solution expressed from cement pastes that contained admixed chloride (mainly calcium chloride). Cement paste specimens were prepared by using OPC and a w/c ratio of 0.5 and calcium chloride from 0.05 to 2% by weight of cement was added to the mixing water. Cl^-/OH^- ratios were determined on solution samples obtained by pore water expression. The reported values were in the range of 0.02...3.14. Diamond also reevaluated the results of Gouda [19]: From the original data given in terms of a plot of the logarithm of critical sodium chloride concentration versus pH he estimated Cl^-/OH^- threshold ratios. The converted results yielded threshold ratios from 0.57 at pH = 11.75 to 0.30 at pH = 13.3. With regard to a high alkalinity in the concrete pore solution the author suggested a critical Cl^-/OH^- ratio of 0.30, which is more conservative compared to the one of 0.6 proposed by Hausmann in 1967 [18]. Diamond reported that the admixture of 0.5% calcium chloride by weight of cement resulted in a Cl^-/OH^- ratio of 0.32 and thus is near the estimated boundary (based on Gouda's results) beyond which depassivation of embedded steel is likely.

Byfors [34] investigated the effect of different types of cement (OPC, SF, FA) on pH values of the pore solution in cement paste samples. Small specimens with a diameter of 19 mm were cast and cured for 14 months in saturated $\text{Ca}(\text{OH})_2$. Disks of 3 mm thickness were then cut from the samples and placed in diffusion cells (exposure to NaCl). The pH value was determined in expressed pore water. Relationships between chloride threshold values and the OH^- concentration reported by Hausmann [18] and Gouda [19] were used to make an estimate of chloride threshold values based on the pH measured in this study. For OPC, a chloride threshold of 0.07 mol/l was calculated. As both the addition of FA and SF decreases the pH of the pore solution, also lower critical chloride contents were derived from Gouda's and Hausmann's relationships: for FA containing cement the estimated threshold was 0.04...0.05 mol/l and for SF containing cement 0.02...0.04 mol/l. Hussain *et al.* [95] measured the hydroxide and chloride ion concentrations in the pore solution pressed out of hardened cement pastes and calculated critical chloride concentrations by assuming a threshold of $\text{Cl}^-/\text{OH}^- = 0.3$. Specimens with w/c = 0.6 were prepared using different cement types (low C_3A , high C_3A content) and various levels of admixed chloride contents. After curing, pore solutions were extracted from the specimens and chemically analysed. It has been found that C_3A affects the Cl^-/OH^- in the pore solution beneficially, *i.e.* the Cl^-/OH^- ratio decreased with increasing C_3A content. By assuming a threshold ratio of 0.3 the concerning chloride contents were calculated.

5.1.3 Other studies related to chloride threshold values

Andrade and Page [54] investigated the effect of cation type on the pore solution chemistry and corrosion in OPC and GGBS cement pastes ($w/c = 0.5$). The chloride and hydroxyl concentrations were determined by pore solution expression from hydrating paste samples that contained different levels of mixed-in NaCl and CaCl₂. In some specimens abraded and cleaned (in acetone) mild steel rods had been embedded and LPR measurements were conducted daily. It was found that after 28 days nearly all of the steel rods appeared to passivate and the initially high current densities decreased below $0.1 \dots 0.1 \mu\text{A}/\text{cm}^2$. The correspondingly reported Cl⁻/OH⁻ ratios were 0.12...0.69 in the case of OPC and 0.16...0.31 in the case of GGBS. Since the steel rods were considered to be passive after 28 days, no chloride threshold values can be derived from the results, but it is indicated that the threshold is higher than the presented values.

Table 4. Published data on critical chloride levels required to initiate corrosion (laboratory conditions)

<i>Investigations under laboratory conditions</i>						SRPC = sulphate resistant Portland cement / RHPC = rapid hardening Portland cement / FA = fly ash containing cement / etc					
Reported chloride threshold			Experimental details						Depassivation detection	Year	Reference
Total Cl ⁻ (% cement wt)	Free Cl ⁻	Cl ⁻ /OH ⁻	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Oxygen availability			
–	–	0.5...1.08 (0.6)	Na	in solution	alkaline solution	–	smooth, cleaned	submerged (but aerated)	potential, visual inspection	1967	Hausmann [18]
0.4	–	–	Ca	mixed-in	mortar (0.45)	OPC	smooth	65% RH	visual inspection	1969	Richartz [4]
–	–	– ^a	Na	in solution	alkaline solution	–	smooth, cleaned	submerged (but aerated)	anodic polarisation, potential	1970	Gouda [19]
3.0	–	–	(seawater)	mixed-in	concrete (0.6)	OPC	smooth	exposure to air	anodic polarisation, potential	1970	Gouda and Halaka [46]
1.0						GGBS					
2.4	–	–	(seawater)	mixed-in	mortar suspension	OPC	smooth	submerged (but aerated)	anodic polarisation, potential	1970	Gouda and Halaka [46]
1.2						GGBS					
0.4...0.8	–	–	Na	mixed-in	concrete (0.4)	OPC	ribbed, cleaned	exposure to air	LPR	1980	Locke and Siman [84]
0.25...0.5	–	–	Ca	mixed-in	mortar (0.5)	OPC	sandblasted	submerged / 60% RH	EIS, visual inspection	1986	Elsener and Böhni [79]
0.1...0.19	–	–	Ca, (Na)	mixed-in	concrete (0.45)	OPC	polished	exposed to air	LPR, EIS, visual inspection, weight loss	1987	Hope and Ip [85]

^a Gouda reported no specific threshold, but a linear relation between the pH and the logarithm of the chloride concentration, see eq. (1)

<i>Investigations under laboratory conditions</i>						SRPC = sulphate resistant Portland cement / RHPC = rapid hardening Portland cement / FA = fly ash containing cement / etc						
Reported chloride threshold			Experimental details						Depassivation detection	Year	Reference	
Total Cl ⁻ (% cement wt)	Free Cl ⁻	Cl ⁻ /OH ⁻	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Oxygen availability				
–	–	7...45	Na	mixed-in / diffusion	mortar (0.5)	OPC	polished	submerged (but aerated)	LPR, potential	1988	Yonezawa et al. [25]	
–	–	4.9	Na	in solution	synthetic pore solution	OPC	polished	submerged (but aerated)	LPR, potential	1988	Yonezawa et al. [25]	
–	–	0.25...0.8	Na, Ca	in solution	synthetic pore solution	–	cleaned	submerged	LPR, potential	1990	Goñi and Andrade [61]	
0.4...1.37	–	–	Na, Ca	diffusion	mortar (0.4...0.6)	OPC, FA, SRPC, SF, RHPC	smooth, cleaned	submerged until corrosion initiation	current between WE and passive external CE	1990	Hansson and Sørensen [27]	
0.5...2.0	–	–	Na	mixed-in / diffusion / capillary suction	concrete (0.4...0.6)	OPC, FA, SF, GGBS	not reported	exposure to air	macrocell current	1990	Schiessl and Raupach [86]	
1.5...2.5	–	3...20	Na	capillary suction and diffusion / (mixed-in)	cement paste / concrete (0.5)	OPC, SRPC	smooth, cleaned	exposure to air (wet/dry cycles)	LPR, potential	1991	Lambert et al. [62,63]	
0.5...1.8	0.36...3.22 mole/l	–	Na	capillary suction and diffusion / mixed-in	mortar (0.4...0.6)	OPC, SF, FA	cleaned	exposure to air	LPR	1992	Pettersson [88]	
–	0.14...1.8 mole/l	2.5...6	Na	diffusion / capillary suction	mortar and concrete (0.3...0.75)	OPC, SF	ribbed	exposure to air	LPR	1995	Pettersson [35]	
–	0.14 mole/l	–	Na	in solution	alkaline	–	ground	submerged	anodic polarisation	1996	Mammoliti et al. [50]	

Investigations under laboratory conditions						SRPC = sulphate resistant Portland cement / RHPC = rapid hardening Portland cement / FA = fly ash containing cement / etc					
Reported chloride threshold			Experimental details						Depassivation detection	Year	Reference
Total Cl ⁻ (% cement wt)	Free Cl ⁻	Cl ⁻ /OH ⁻	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Oxygen availability			
	0.28 mole/l				solutions		ribbed				
	0.42 mole/l						polished				
0.5...1.0	-	-	Na	mixed-in / diffusion	concrete (0.5...0.7)	OPC	ribbed	exposure to air	macrocell current	1996	Schiesl and Breit [47]
1.0...1.5						GGBS, FA					
-	0.44...0.65 mole/l	-	Na	capillary suction and diffusion	mortar (0.75)	OPC	not reported	submerged	potential	1997	Elsener et al. [75]
-	0.056 mole/l	0.26	Na	in solution	synthetic pore solution	-	cleaned	submerged	potentiostatic control	1998	Breit [11]
0.25...0.75	(0.1...? mole/l)	-	Na	diffusion	mortar (0.5...0.6)	OPC, SF, FA, SRPC, GGBS	smooth	submerged	potentiostatic control, visual inspection	1998	Breit [89]
1.24...3.08	0.39...1.16% cem wt	1.17...3.98	Na, (Ca)	mixed-in	mortar (0.5)	OPC	ribbed and smooth	100% RH	LPR, potential	2000	Alonso et al. [14]
-	-	0.7...1.7	Na	in solution	synthetic pore solution	-	sandblasted, cleaned	oxygen supply	potential, macrocell current	2000	Zimmermann et al. [15,91]
0.25...1.25	0.045...0.55 mole/l	-	Na	capillary suction / diffusion	mortar (0.6)	OPC	sandblasted, cleaned	exposure to air	potential, macrocell current	2000	Zimmermann et al. [15,91]
-	-	0.01...2.5	Na	in solution	alkaline solutions	-	as received, sandblasted, pre-rusted	submerged	potential, EIS	2001	Li and Sagüés [51]
0.73	0.50% cem wt	1.76±0.3	Na	diffusion	mortar (0.5)	OPC, SRPC, FA	ribbed, mill-scaled	submerged	potentiostatic control	2002	Alonso et al. [23]

Table 5. Published data on critical chloride levels required to initiate corrosion (outdoor exposure conditions)

<i>Investigations under outdoor exposure conditions</i>						SRPC = sulphate resistant Portland cement / RHPC = rapid hardening Portland cement / FA = fly ash containing cement / etc					
Reported chloride threshold			Experimental details						Depassivation detection	Year	Reference
Total Cl ⁻ (% wt of binder)	Free Cl ⁻	Cl ⁻ /OH ⁻	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Oxygen availability			
0.2...1.4			Na, (Ca)	mainly de-icing salts	various	various	not reported	exposed to air	potential	1975	Stratfull et al. [83]
0.1...0.19	–	–	Ca, (Na)	mixed-in	concrete (0.45)	OPC	polished	exposed to air	LPR, EIS, visual inspection, weight loss	1987	Hope and Ip [85]
0.7	–	–	(seawater)	capillary suction and diffusion	concrete (0.32...0.68)	OPC	ribbed	tidal zone (marine exposure)	weight loss	1996	Thomas et al. [38,87]
0.2...0.65						FA					
0.4...1.5	–	–	(seawater)	diffusion	concrete (0.3...0.75)	SRCP, FA, SF, GGBS	ribbed, as received	exposure to seawater	potential, (LPR, galvanostatic pulse)	1998	Sandberg [90]
0.2...0.4	–	–	Na	diffusion	concrete	OPC	not reported	not clearly reported	macrocell current	2000	Zimmermann [15]

5.2 Evaluation of reported values

5.2.1 Total chloride threshold values

In Fig. 6 reported chloride threshold values expressed in the form of total chloride by weight of binder are shown. Due to the differences in methodology and definition in the reviewed publications and the variety of influencing parameters it is difficult to compare the obtained results. However, the following tendencies can be seen:

Generally, a very high overall scatter was found: the reported values range from 0.02 to 3.08% total chloride by weight of cement and thus over two orders of magnitude. This is in line with other literature reviews, where also a high scatter was found [10,13].

As the steel potential is one of the major influencing factors the reported values have been grouped according to the measured potentials. As a border a value of -200 mV SCE has been assumed based on the findings presented in ref. [23]. In many studies, the initial potential was higher than

-200 mV SCE. In some publications, no potentials were measured or reported, but in most of these cases the exposure conditions described in the publications indicate that the steel potentials presumably were in the same range. In two publications, the steel potential was below -200 mV SCE and significantly higher chloride threshold values were reported accordingly.

If only the values from studies performed at potentials presumably higher than -200 mV SCE are considered, a higher scatter can be found for the concrete specimens in comparison with the mortar specimens. Surprisingly, also a slight tendency for higher critical chloride contents for concrete specimens in comparison with mortar specimens can be derived from Fig. 6. It is however not significant. Any other influences such as the type of rebar used (smooth vs. ribbed), the chloride introduction (mixed-in vs. introduced later) or the type of cement cannot be identified from these data.

5.2.2 Cl^-/OH^- threshold ratios

Fig. 7 shows reported chloride threshold values expressed in the form of Cl^-/OH^- ratios. As the values span a large range they have been divided into two separate plots with different scaling on the ordinate. Again, a high overall scatter can be found from the smallest value 0.03 to the maximum at 45; by this, the values range over three orders of magnitude.

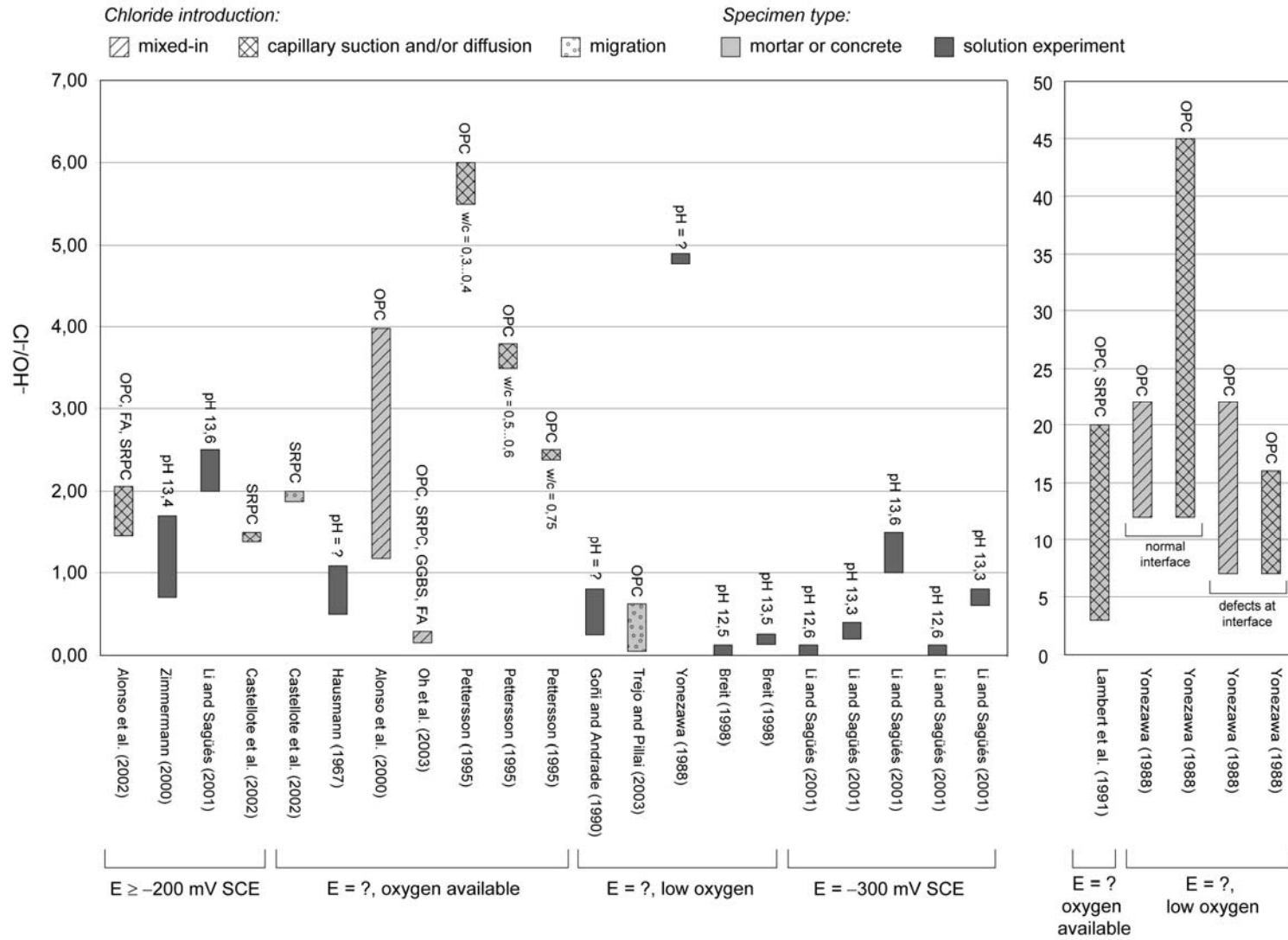
It is evident from **Fig. 7** that the values obtained from experiments dealing with concrete or mortar specimens scatter much more than those from experiments performed in solutions.

Most authors haven't reported the steel potential. However, in **Fig. 7** the evaluated results have been split into several groups: a) experiments carried out at potentials more positive than -200 mV SCE, b) potentials not reported and c) potentials more negative than -200 mV SCE. As the publications gave some information on moisture and oxygen availability during the experiments, the values without known potentials have been split into studies where the steel surface was aerated during the experiments and studies with submerged steel electrodes (low oxygen). From the evaluated results no relationship between potential and critical chloride content can be derived.

Fig. 7 depicts higher chloride threshold levels for studies dealing with mortar or concrete specimens in comparison with solution experiments. This might be explained by the inhibiting effects of the interface of steel embedded in a cement matrix, especially due to formation of a Portlandite layer at the steel surface [17]. This is the only influencing factor that has a dominating effect on the critical chloride content and clearly appears in the evaluated data.

Unfortunately, many authors haven't measured or reported the pH and thus it is not possible to see the overall effect of the alkalinity on pitting initiation from the evaluated results in **Fig. 7**. Only from the results obtained by Li and Sagüés (2001) [51] and Breit (1998) [11] it can be seen that the Cl^-/OH^- threshold ratio increases with increasing pH of the pore solution.

Fig. 7. Comparison of reported threshold values presented as Cl^-/OH^- ratios



5.2.3 Comparison of different forms to express the critical chloride content

In order to compare the different possibilities to express critical chloride contents, studies in which more than one form was determined have been evaluated. The span of the reported values is expressed by giving the percentage of the minimal value to the maximum value as depicted in Fig. 8. In the diagram, higher columns indicate a higher span. The according values for total chloride and Cl^-/OH^- ratios are given in Table 6. This allows comparing the reported ranges of different threshold value forms.

In their literature review published in 1997, Glass and Buenfeld [13] evaluated data reported by Lambert *et al.* [62] and pointed out that Cl^-/OH^- ratios span a larger range in comparison with corresponding total chloride contents. As can be seen from Table 6 and Fig. 8, some studies published later confirm this, whereas the values reported by Castellote *et al.* (2002) [92] and Oh *et al.* (2003) [93] indicate the opposite and the results of Trejo and Pillai (2003) [80] do not show any differences. If all of the reported values evaluated in this work – summarised in Table 4 and Table 5 – are considered, a higher range is found for Cl^-/OH^- ratios in comparison with total chloride contents: Threshold values expressed as total chloride range from 0.02 to 3.08% with the minimum being equal to 0.65% of the maximum value; for Cl^-/OH^- ratios the span is 0.01...45 with the minimum being equal to 0.02% of the maximum value. The Cl^-/OH^- values range over three orders of magnitude, whereas this is two orders of magnitude for the total chloride threshold values. Glass and Buenfeld [13] suggested that this might be explained by the non-linear relationship between bound (total) and free chlorides; any scatter in bound chloride is amplified when expressed as a free chloride content. Another reason could be the fact that the determination of the total chloride content is the most accurate since it is well established and documented in standards, whereas for the determination of free chloride concentrations, various procedures attributed with different inaccuracies have been applied (Fig. 8).

However, if the chloride threshold values are reported in the form of free chloride content, sometimes higher (Pettersson (1992) [88], Alonso *et al.* (2000) [14] and Zimmermann (2000) [15]) and sometimes lower (Castellote *et al.* (2000) [92] and Oh *et al.* (2003) [93]) values than the corresponding total chloride contents were reported.

Three publications were found in which the critical chloride content was reported in the form of total chloride, free chloride and as Cl^-/OH^- ratios: Alonso *et al.* (2000) [14], Castellote *et al.* (2000) [92] and Oh *et al.* (2003) [93]. In this context, Fig. 8 reveals no systematic tendency for the range of the forms in which the critical chloride content is expressed; these three studies show three different combinations.

No new conclusion can be drawn from this comparison apart from the one already mentioned by Glass and Buenfeld [13]: Since only the free chloride is considered to initiate corrosion, forms to express the chloride content that ignore bound chloride such as Cl^-/OH^- ratios or free chloride by mass of cement should theoretically result in a smaller range of values. This obviously is not always the case. Glass and Buenfeld thus suggested that also the bound chloride may present a corrosion risk and the threshold is best expressed as total chloride by weight of cement.

5.2.4 Summary of reported threshold values

To sum up, different techniques and experimental setups have been used by various authors. The interaction of many influencing factors is complex and the effect of single parameters, such as *e.g.* the type of cement, cannot be identified from the evaluated results. The only influencing factor which appears to have an overall effect is the condition of the steel-concrete interface, as for experiments conducted in alkaline or synthetic pore solutions, generally lower threshold values have been reported in comparison with studies dealing with mortar or concrete samples. This can also be seen from the results of Yonezawa *et al.* [25], where the steel-concrete interface was deliberately produced in a normal and a bad (no Portlandite at the steel surface) condition. From certain studies it is possible to identify the beneficial influence of a higher pH value on the critical

chloride content [11,51]. It is also evident from some publications that at potentials more negative than -200 mV SCE generally higher total chloride threshold values were reported. This is, however, only partially supported by evaluated studies in which the threshold values were expressed in the form Cl^-/OH^- ratios.

From the evaluated data no specific form to express the critical chloride content is favoured. The scatter in the reported values is relatively high in all of the three forms (total chloride, free chloride, Cl^-/OH^- ratio) and no tendency towards lower scatter for a certain expression form is evident (Fig. 8).

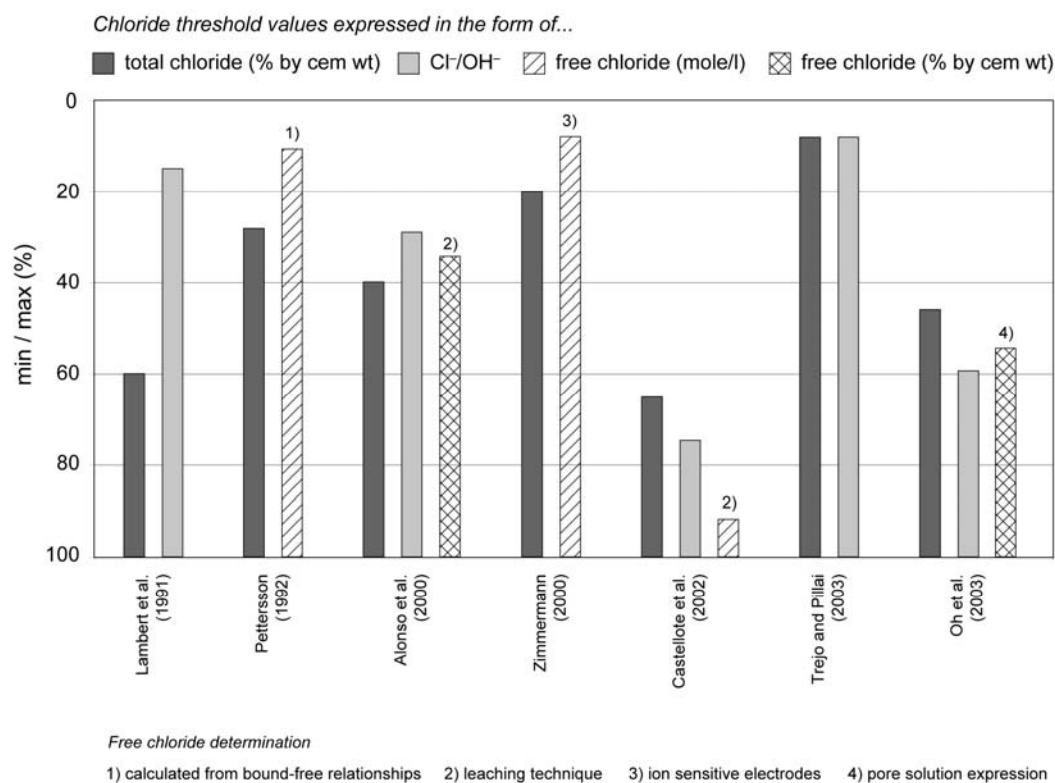


Fig. 8. Ranges of reported threshold values expressed in different forms

Table 6. Range of published threshold values expressed as total chloride and Cl^-/OH^- ratios

Study	Range of total chloride	Range of Cl^-/OH^- ratio
Lambert et al. (1991) [62]	1.5...2.5% cement weight 60...100%	3...20 15...100%
Alonso et al. (2000) [14]	1.24...3.08% cement weight 40...100%	1.17...3.98 29...100%
Alonso et al. (2002) [23]	0.73% cement weight	1.76
Castellote et al. (2002) [92]	0.15...0.23% cement weight 65...100%	1.5...2.0 75...100%
Trejo and Pillai (2003) [80]	0.02...0.24% cement weight 8...100%	0.05...0.62 8...100%
Oh et al. (2003) [93]	0.45...0.97% cement weight 46...100%	0.16...0.27 59...100%

5.3 Testing methods

As was presented in section 4 a variety of test setups is possible in order to investigate the critical chloride content of steel in concrete. Fig. 9 shows the possible combinations and the percentages of application evaluated based on the present literature review. It has been tried to include as many references as possible in order to cover a representative proportion of the published data. As only the free chloride ions in the pore solution are considered to initiate pitting corrosion, in many studies solution experiments have been performed. By this, the system “steel embedded in concrete” is reduced to steel in a solution. Also the concept of representing the inhibitive properties of the concrete by the hydroxide ion concentration and the destructive species by the free chloride ion concentration as Cl^-/OH^- ratio supports solution experiments. In around 30% of the studies evaluated in the present literature review experiments were performed in alkaline solutions or cement suspensions (Fig. 9).

Besides the pH of the pore solution also the properties of the steel concrete interface have been identified to significantly influence the critical chloride content. This can only be taken into account by using concrete (or mortar) specimens containing a steel bar. Also the type of rebar (ribbed or smooth) as well as the surface condition (*e.g.* sandblasted or prerusted) has an effect on the quality of the steel concrete interface. Although in some studies these conditions were not reported, it can be seen from Fig. 9 that a majority of experiments has been performed with smooth steel and that cleaning procedures such as rinsing in acetone, sandblasting or polishing have been applied frequently.

In approximately a third of the evaluated studies chloride has been admixed initially. In case of chloride introduction into hardened concrete diffusion or a combination of capillary suction and diffusion have often been applied, whereas accelerated chloride ingress by migration has only been used rarely. For solution experiments, it is very common to add chloride with increasing steps in concentration after an initial chloride free resting time. Against the background of accelerators based on calcium chloride, in many investigations chloride has been added in the form of calcium chloride. After ca. 1990, mostly sodium chloride and in some cases seawater have been investigated.

In order to detect depassivation the potential of the steel, LPR measurements or monitoring of the current in *e.g.* experiments under potentiostatic control are the most frequently applied techniques. Circa 50% of the reported threshold values evaluated in this work were expressed in the form of total chloride by weight of cement or concrete. Also Cl^-/OH^- ratios and free chloride concentrations have been reported frequently.

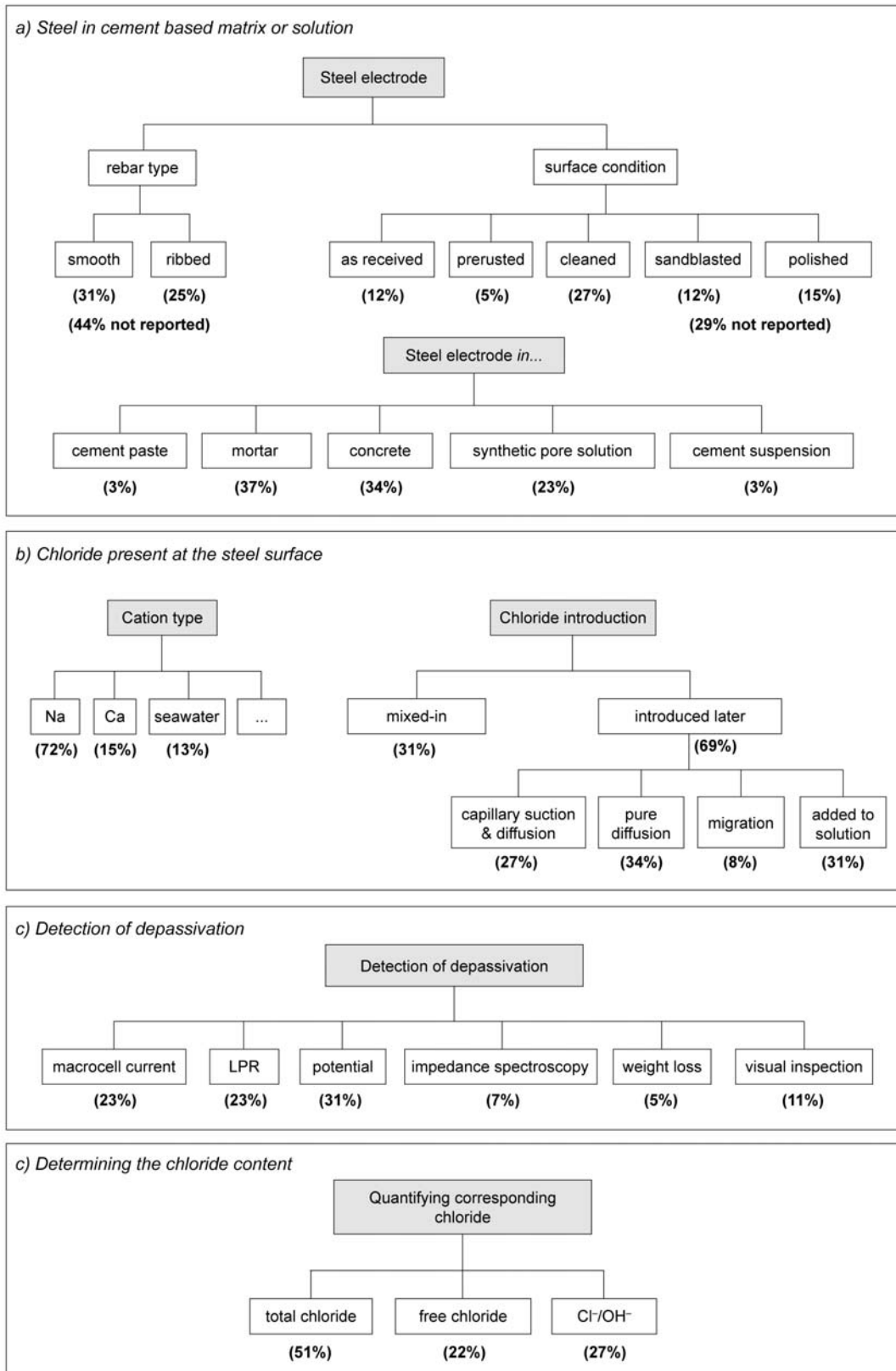


Fig. 9. Possibilities to study critical chloride content (percentages of application based on the present literature review given in brackets)

6 Conclusions

From this literature review on measurement techniques and publications dealing with the issue of critical chloride content, the following major conclusions can be drawn:

1. A lot of studies have been undertaken in the context of critical chloride content and the published results scatter in a wide range. The reported results span from 0.02 to 3.08% total chloride by weight of binder and thus over two orders of magnitude. Published Cl^-/OH^- ratios even range from 0.03 to 45 and thus over three orders of magnitude.
2. The concept of critical chloride content is a complex matter and the onset of pitting corrosion in the presence of chloride is determined by a lot of influencing factors. Most of these factors are also interconnected and variable with time. Major influences are the quality of the steel-concrete interface, the potential of the steel and the pH of the pore solution. Other factors with direct or indirect influence are the moisture content in the concrete, the composition of the steel, the type of cement, w/c ratio, temperature, etc.
3. From the evaluation of results available in literature the most dominating influencing factor appears to be the steel-concrete interface: For experiments conducted in alkaline or synthetic pore solutions, generally lower threshold values have been reported compared to studies dealing with mortar or concrete samples.
4. From certain solution experiments it is evident that a higher pH value has an inhibiting effect and higher amounts of chloride can be tolerated accordingly. Also the effect of the steel potential has been detected from the evaluated publications: At potentials below -200 mV SCE much higher total chloride threshold values have been reported. This is, however, not supported by data obtained in the context of threshold values expressed in the form of Cl^-/OH^- ratios. Any other influences could not be detected from the totality of the evaluated results; due to complex interaction of the effects of multiple parameters it was not possible to distinguish single factors such as *e.g.* the type of cement or w/c ratio.
5. Experimental investigation of the issue of critical chloride content can be performed in a wide variety of possible procedures. The multiplicity of parameters includes rebar type (smooth or ribbed), steel surface condition (as received, sandblasted, etc), matrix (cement paste, concrete, alkaline solutions, etc), chloride introduction procedures (mixed-in, diffusion, migration, etc), depassivation detection techniques (LPR, potential, weight loss measurements, etc), chloride quantification methods (total chloride, free chloride by pore solution expression and pore water analysis, leaching techniques, etc). At present, there is no generally accepted or standardised procedure for the determination of the critical chloride content.
6. A lot of studies have dealt with critical chloride content by quantifying the total chloride content in both mortar and concrete samples or by measuring the free chloride content in solution experiments and mortar or porous concrete. Up to now, there is a lack of information on concrete of higher quality (low w/c ratio, alternative cement types) on the basis of the free chloride content. This may be mainly because of the difficulties in measuring the free chloride content in dense concrete. Moreover, many studies have used mixed-in chloride, although the initial presence of chloride might

hinder the formation of a passive layer and thus affect the corrosion behaviour. In the majority of studies the steel bars were prepared (cleaned, sandblasted, etc) prior to the investigation that was conducted either in a cement based material or in synthetic pore solutions. In many cases the conditions at the steel-concrete interface can thus not be considered as realistic; as was shown this affects the critical chloride content.

7. It is widely accepted that no unique chloride threshold value exists. Thus in modern service life prediction the critical chloride content is considered as a stochastic variable characterised by a mean value, a standard deviation and a type of probability density function. However, due to lacking reliable information conservative values or high standard deviations are used. Further research is needed to establish a database of reliable chloride threshold values that can be used as input parameters for service life modelling.

7 Future research

Although a lot of studies have already been performed, there is still a need for more knowledge in the field of chloride induced corrosion. Complex mathematical models are available for service life predictions, but for the input parameter *critical chloride content* still vaguely defined and often conservative values are used. Results are missing mainly for concrete of higher quality (low porosity) in connection with the amount of free chloride. The need for further research is also indicated by on-going research programmes such as the COIN subproject no. 4.2 “critical chloride content and corrosion process”.

Future work could include the following:

- Establish a procedure for determining critical chloride content. The comparability of the so far reported results is very difficult, mainly due to use of different methods for detecting depassivation and measuring the chloride content. If agreement on measurement techniques was reached, future results of different authors could be compared and the scatter in reported results reduced.
- There is still a lack of results in the range of low porosity concrete and reliable data concerning free chloride content. Experimental work is needed to fill this gap by focusing on high performance concrete with different types of cement and relatively low w/c ratios, as well as on the free chloride content at the steel surface. This could also provide a better understanding on the roles of bound and free chlorides in the corrosion initiation process. So far, studies reporting chloride threshold values as both total chloride and free chloride (or Cl^-/OH^- ratios) were confusing with regard to the importance of bound chloride in the corrosion initiation process.
- Establish a database with reliable chloride threshold values in order to perform reasonable service life predictions. By this, the consultant performing the service life calculation could assess critical chloride contents by taking into account concrete properties and environmental factors. The data should be based also on experience from real structures.

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