



Chloride Threshold Values

State of the art

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1 Introduction

It is widely recognized that the ingress of chlorides into concrete can initiate reinforcement corrosion and ultimately result in deterioration of the concrete structure under chloride attack. The importance of chloride induced corrosion is reflected by the extensive number of scientific publications that has previously been dedicated to this phenomenon.

A crucial input parameter for the modelling of the service lifetime of reinforced concrete structures is the so-called chloride threshold value, which may be defined as the minimum concentration of chloride at the depth of the reinforcement that is able to initiate corrosion of the steel. Without an experimentally determined chloride threshold value engineers are generally forced to make rather conservative guesses about this value, thus potentially underestimating the service lifetime dramatically.

Reported chloride threshold values in the literature display a wide scatter, which is due to the fact that: (1) numerous different experimental approaches have been employed to obtain the chloride threshold value, and (2) the chloride threshold value is influenced by numerous different parameters. In order to make reasonable and scientifically sound comparison of experimentally determined chloride threshold values, a generally accepted test method for determination of this parameter is greatly needed. Presently, such a method is still lacking.

The present *state of the art* report is based on a literature study on the topic of 'chloride threshold values', which has been carried out as part of a current project concerned with the development of a useful and fast in-lab reference method for determination of chloride threshold values. The project is associated with the Danish Expert Centre for Infrastructure Constructions, Danish Technological Institute and the literature study was done in order not to repeat research work and experiments that have already been performed by other researchers. The study was also undertaken in order to obtain an overview of the challenges/pitfalls within this research area, as well as to identify where future research might be needed.

This report presents the most important parameters affecting the chloride threshold and gives a review of available experimental methods for quantification/detection of chloride in concrete and techniques for detection of reinforcement corrosion. A section is also devoted to the presentation of chloride threshold values from the literature and finally the report addresses the work of a RILEM committee (TC 235 CTC), which is concerned with the development of a generally accepted test method for determination of chloride threshold values in concrete.

It is noted, that the main reason for preparing this report, was an internal need within the Expert Centre to obtain a general overview of the most important findings from essential re-

search carried out in relation to the topic of 'chloride threshold values'. The reader is referred to the report by Angst & Vennesland [2007] for a more detailed and comprehensive review of the topic.

2 Chloride threshold value

2.1 Definition of chloride threshold value and general concepts

Chloride induced corrosion is a concern in relation to reinforced concrete structures exposed to seawater or if the structure is exposed to de-icing salts (e.g. bridges during the winter). By the action of wind and rain, the salt is moved to other parts of the structure where scaling may occur through evaporation processes. This is mainly true for concrete of poor quality with high water/cement ratios, and is generally not a concern for good quality concrete prescribed for an aggressive environment.

Once the chloride ions have reached the surface of the concrete they can subsequently penetrate the concrete cover and reach the reinforcement where they act as catalysts for the corrosion process at the steel surface. Reinforcing steel is normally passivated (i.e. the corrosion rate is insignificant) in concrete due to the alkaline nature of the pore solution, which promotes the formation of a barrier "film" consisting of iron oxides on the surface of the steel. However, the steel can become depassivated provided that a certain threshold concentration of chloride ions is reached at the steel surface. The chloride threshold value may thus be defined as the minimum concentration of chloride at the depth of the reinforcement, which results in active (pitting) corrosion of the steel. It has also been suggested that the chloride threshold value may be defined as the chloride concentration at the steel surface at the time when deterioration or damage of the concrete commences [Schiesl et al., 1982]. However, the first definition is applied exclusively in this report. Sometimes *chloride threshold value* is also referred to as *chloride threshold level*, *critical chloride content* or *chloride threshold concentration*.

According to a very popular model put forth by Tuutti [1982] the service life of reinforced concrete may be separated into two periods (Figure 1). During the initiation period the reinforcing steel remains passivated, but as the chloride threshold value is reached at the steel surface, localized (pitting) corrosion begins, thus marking the transition to the so-called propagation period in which active corrosion occurs. However, the service lifetime of a reinforced structure is also often regarded as being equal to the duration of the initiation period, but this might not be appropriate, since it is very unlikely that all of the reinforcement will begin to corrode at the same time.

The service lifetime may instead be more conveniently defined as the time at which a certain fractile (for example the 5%-fractile) of the structure in an inspection zone has started to cor-

rode [Nilsson et al., 1996]. On the other hand, rather localized corrosion can also become hazardous if the reinforcement of a particularly critical cross-section of the concrete structure is severely corroded.

When trying to estimate the service lifetime of a reinforced concrete structure two main parameters must generally be considered: (1) Chloride transport processes through the concrete and (2) the conditions required for corrosion initiation (chloride threshold value). Traditionally, the first of these two parameters has received the largest share of attention in the literature, but without an appropriately chosen chloride threshold value the estimated duration of the service lifetime becomes rather meaningless. It is therefore very important to be able to experimentally determine the chloride threshold value in a reliable manner. Unfortunately, a generally accepted method for determination of the chloride threshold value in reinforced concrete is still lacking.

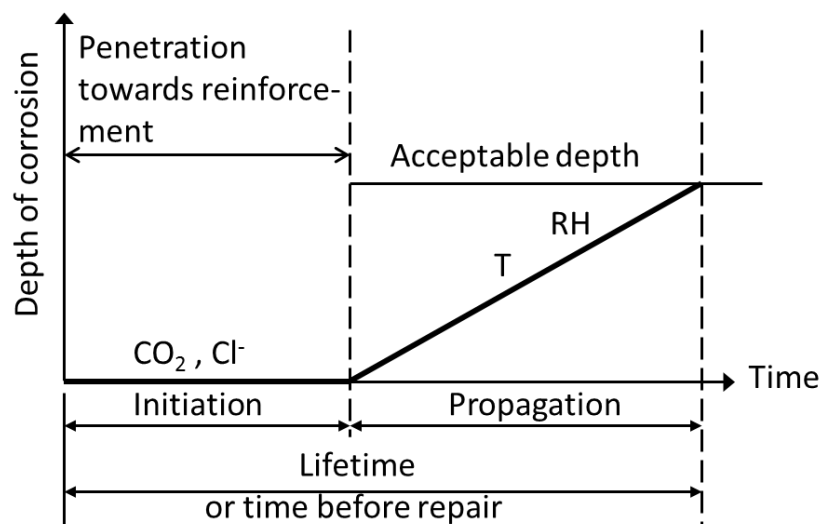


Fig. 1 Schematic sketch of Tuutti's model for the service lifetime of reinforced concrete. Modified after Fig. 1 in Tuutti [1982].

2.2 Influential parameters

The passivity of reinforcing steel in concrete is influenced by a wide range of factors, as illustrated in Figure 2. Similarly, the chloride threshold value for corrosion initiation on reinforcing steel in concrete is influenced by several different parameters, the most important of which are presented in the following.

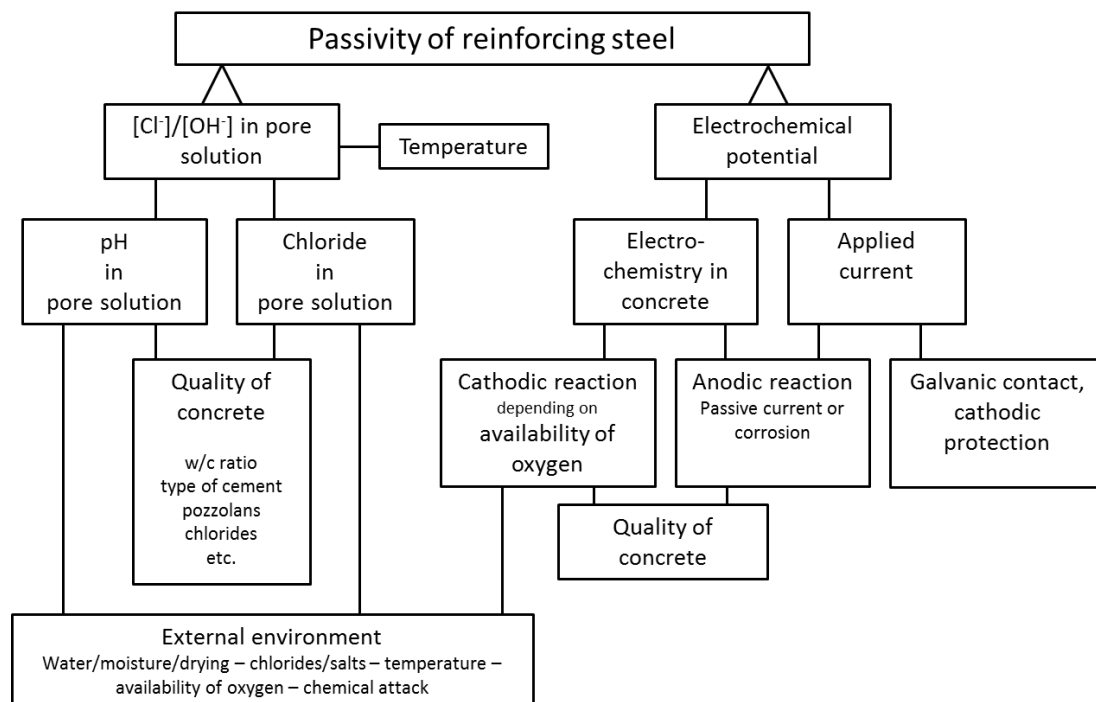


Fig. 2 Diagram showing the wide range of factors, which influence the passivity of reinforcing steel in concrete. The figure is a modified version of Fig. 1 in [Arup, 1993].

2.2.1 pH of pore solution

Typically, the pore solution of concrete has a pH-value above 12.6 due to the presence of portlandite ($\text{Ca}(\text{OH})_2$), and even higher values can be observed for concrete rich in NaOH and KOH. The highly alkaline environment of the pore solution favors the formation of a passive oxide film on the surface of the steel reinforcement and a high pH-value is therefore an important inhibiting factor with regard to corrosion initiation [Angst and Vennesland, 2007]. It should be noted that the pH of the pore solution may change with time as a consequence of phenomena such as carbonation (see section 2.2.2) or continued hydration reactions of the binder components.

In addition to the inhibiting effect on corrosion initiation, the pH may also affect the binding of chlorides. Studies have shown that a reduction of the pH to a value below 12.5 results in the release of a considerable part of the bound chlorides, while yet another part is released

if the pH value is reduced to a value around 12 [Glass et al., 2000; Reddy et al., 2002]. The release of bound chlorides has been ascribed to the dissolution of Friedel's salt and C-S-H phases as a result of reduced alkalinity.

Based on experiments with steel bars in synthetic concrete pore solutions, Hausmann [1967] and Gouda [1970] have proposed that the chloride threshold value is most accurately expressed using the $[Cl^-]/[OH^-]$ ratio. These early works suggested a chloride threshold value of about 0.6, a result that was later supported by Tuutti [1982], and it seems well-established that the pH of the pore solution has a major influence on the amount of chloride that leads to initiation of pitting corrosion.

2.2.2 Carbonation

A significant drop in pH of the pore solution accompanies the carbonation of concrete, and the chloride threshold value is virtually reduced to zero if the carbonation process reaches the depth of reinforcement [Nilsson et al., 1996]. This is due to the fact that steel is not passive in the pH environment associated with carbonated concrete, and pitting corrosion is thus easily initiated when chloride is present. The corrosion process is further promoted by carbonation since the chloride binding capacity of the binder is reduced by the carbonation, which subsequently leads to an increase in the concentration of free chlorides in the pore solution. It should be noted, that the corrosion of steel reinforcement can also occur in carbonated concrete even if chloride ions are not present in the pore solution, because the protective oxide film on the steel surface is generally depassivated at the pH value associated with carbonated concrete.

2.2.3 Water/binder ratio

Experimental data have indicated that concretes with lower water/binder ratios exhibit higher chloride threshold values as compared to concretes having higher water/binder ratios [Pettersson, 1992, 1994; Schiessel and Breit, 1995] (Figure 3). This is most likely due to the following consequences of a low water/binder ratio [Nilsson et al., 1996]:

- Reduced area available for development of pitting corrosion caused by a denser steel-concrete interface.
- Higher resistivity of the concrete.
- Lower chloride mobility resulting in a reduction of the catalytic effect of the chloride ions.
- Improved ability to maintaining a high alkalinity of the pore solution due to a reduced leaching rate for alkalis and a buffer of unreacted cement particles.

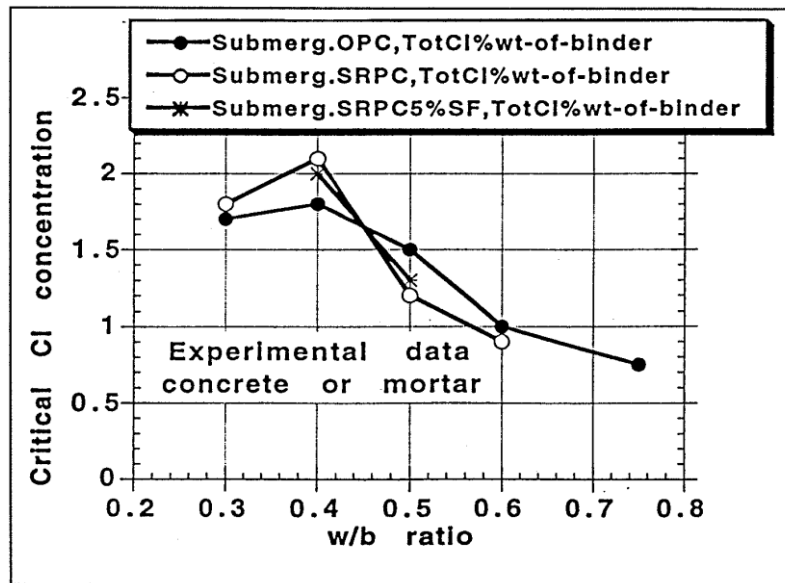


Fig. 3 Experimental data illustrating the influence of water/binder ratio on the chloride threshold value for initiation of corrosion in submerged concrete or mortar. The figure is taken from Nilsson et al. [1996] and based on experimental data from Pettersson [1992, 1993 and 1994].

2.2.4 Type of binder

A survey of the literature reveals rather conflicting results regarding the effect of supplementary cementitious materials on the chloride threshold value. Below, the effect of ground granulated blast-furnace slag, fly ash and silica fume is treated individually, and the effect of different types of Portland cement on the chloride threshold value is presented as well.

- *Ground granulated blast-furnace slag (GGBS)*

Partial replacement of ordinary Portland cement (OPC) with GGBS has been reported to increase the chloride binding capacity of the binder [Arya, 1993; Dhir et al., 1996; Luo et al., 2003]. This is probably due to the relatively high content of alumina in GGBS, which facilitates the formation of additional Friedel's salt. However, the addition of GGBS also has the effect of reducing the pH value of the pore solution [Cheng et al., 2005], which promotes the initiation of pitting corrosion. These two mechanisms (increased chloride binding capacity and reduced pH of the pore solution) have each the opposite effect on the chloride threshold value, thus making it difficult to make general conclusions regarding the overall influence of replacing OPC with GGBS. It should also be mentioned that GGBS can act as an internal chloride source if the production of the GGBS involves quenching in seawater [Neville, 1995].

Both Gauda and Halaka [1970] as well as MacPhee and Cao [1993] have reported reduced chloride threshold values for slag-containing concrete compared to concrete with plain Portland cement. On the other hand, Schiessl and Breit [1996] found higher chloride threshold values for concrete with GGBS compared with concrete without

GGBS. Some studies have also concluded that the addition of GGBS has no effect on the threshold value [Bamforth and Chapman-Andrews, 1994; Thomas et al., 1990].

- *Fly ash*

The addition of fly ash to the binder of concrete has two main influences on the chloride threshold value: (1) The high content of alumina in fly ash increases the chloride binding capacity of the binder [Arya, 1990; Dhir and Jones, 1999], and (2) the pH value of the pore solution is lowered [Byfors, 1987; Diamond, 1981]. As with the addition of GGBS, it is difficult to make generalized conclusions about the effect of fly ash on the chloride threshold value, since the two abovementioned effects inhibit and promote the initiation of pitting corrosion, respectively. In a study on reinforced concrete samples that had been exposed to marine environment for up to four years Thomas [1995] found that the chloride threshold value became progressively lower as the amount of fly ash in the concrete mix increased. Alternatively, Bamforth and Chapman-Andrews [1994] and Thomas et al. [1990] have reported that the addition of fly ash to concrete has no effect on the chloride threshold value. It is also worth noting that a partial replacement of Portland cement by fly ash (or GGBS) results in a refinement of the pore structure of the cement paste, which leads to a higher resistance of the concrete against the ingress of chloride ions [Angst and Vennesland, 2007]. This has no direct influence on the chloride threshold value, but the increased electrochemical resistance will decrease both chloride mobility and macrocell current and thereby probably result in a higher chloride threshold value.

- *Silica fume*

Lower chloride binding capacity have been reported for silica fume-containing cement as compared to pure Portland cement [Page and Vennesland, 1993; Arya et al., 1990]. This may partly be a consequence of the reduced amount of aluminate phases present in a binder where the Portland cement has been partially replaced by silica fume (almost pure SiO_2). Silica fume is a very fine-grained material and its presence as part of the binder in a concrete will lead to a more refined pore structure, which may enhance the physical adsorption of chloride to the surface of the C-S-H gel [Angst and Vennesland, 2007]. However, Larsen [1998] has reported that the C-S-H formed by the pozzolanic reaction of silica fume with portlandite (Ca(OH)_2) may have lower chloride binding properties than C-S-H formed by hydration of pure Portland cement.

The pH value of the pore solution is affected by the addition of silica fume, as the consumption of Ca(OH)_2 results in a decrease of the alkalinity [Byfors, 1987]. This ultimately lowers the chloride binding capacity, since the solubility of Friedel's salt increases with decreasing pH of the pore solution [Page and Vennesland, 1993]. The negative effect of silica fume on the chloride threshold value has been demonstrated experimen-

tally in a number of studies [Hansson and Sørensen, 1990; Pettersson, 1993; Manera, 2007].

- *Effect of Portland cement type*

The choice of cement type indirectly affects the chloride threshold value since the chloride binding capacity of concrete is dependent on the type of cement used in the mix. It seems well established that the chloride binding capacity of Portland cement is highly dependent on the content of C_3A [Schiessl and Raupach, 1990]. For example, the lower binding capacity of sulphate resisting Portland cements (low in C_3A) have been indicated by shorter corrosion initiation time and increased active corrosion rate for these cements as compared to Portland cement high in C_3A [Rasheeduzzafar et al., 1992], but Byfors [1990] found the opposite effect for a sulphate resisting Portland cement rich in ferrite (C_4AF). Furthermore, based on thermodynamic considerations as well as experimental evidence, Nielsen [2004] concluded that amount of alumina in a Portland cement has a relatively minor effect on the chloride binding capacity. Instead, the chloride binding was found to be much more dependent on the content of alkalis, with higher contents of alkalis resulting in lower amounts of bound chlorides.

2.2.5 Oxygen availability and moisture content

Availability of both oxygen and water is required for active pitting corrosion to occur (Figure 4). The corrosion process involves the cathodic reduction of oxygen, and the amount of available water is an important parameter for the distribution between free and bound chlorides. The content of water also determines the chloride concentration and if the concrete is rather dry the electrolytic corrosion process becomes restricted [Angst and Vennesland, 2007].

The transport of oxygen through concrete is dependent on the relative humidity [Tuutti, 1982] and a dramatic reduction in oxygen transport rate can be observed if the pores become saturated. This due to the fact that oxygen diffusion through gas (air) is orders of magnitude higher than diffusion through liquid (water-filled pores). Furthermore, the steel potential in concrete, an important factor when considering the initiation of corrosion, is closely linked to the availability of free oxygen: The steel potential is reduced when the availability of oxygen is limited, which implies that the chloride threshold value is higher for reinforcement in submerged concrete structures as compared to reinforcement in concrete subjected to repeating cycles of drying and wetting. This has been confirmed by experimental result reported by Pettersson [1990].

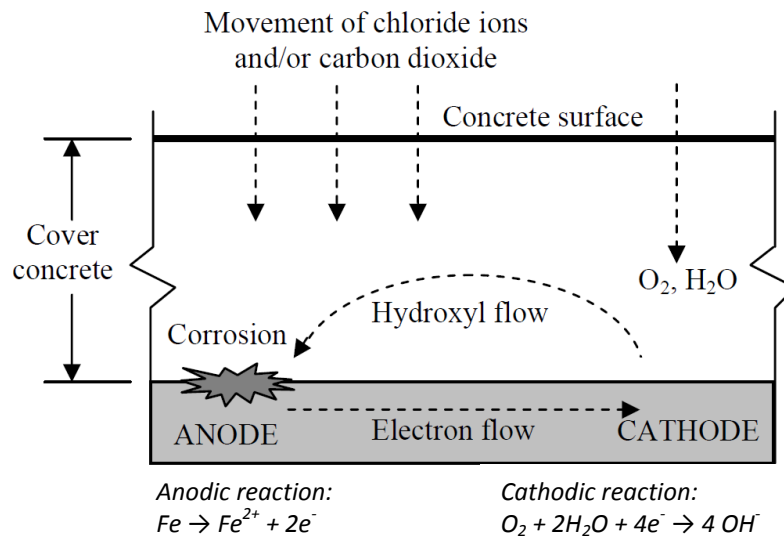


Fig. 4 Schematic illustration of the corrosion process in reinforced concrete, which involves the anodic and cathodic reactions. After Mackechnie et al. [2001].

2.2.6 Temperature

It is well-known that an increase in temperature leads to a reduced corrosion resistance of stainless steel in chloride solutions [Mattsson, 1992]. Correspondingly, it seems reasonable to expect that the chloride threshold value for reinforcement in concrete will decrease with increasing temperature, but direct experimental evidence for such a relationship is lacking.

Hussain and Rasheeduzzafar [1993] have studied the effect of curing temperature on the binding of chloride for a series of cement pastes. Chloride was added through the mix water at three different levels (0.3, 0.6 and 1.2% by weight of cement) and samples were cured for 180 days at either 20 or 70°C. Based on the analysis of extracted pore solutions it was concluded that the amount of unbound chlorides increases with increased temperature. They also found that the concentration of hydroxyl ions in the pore solution decreased with increasing temperature. The $[Cl^-]/[OH^-]$ ratio was therefore found to be considerably higher at 70°C as compared to 20°C, thus indicating an increase in corrosion risk. The activation energy required to break down the passive oxide film on the steel surface may also be affected by the temperature [Glass and Buenfeld, 1995].

2.2.7 Electrochemical potential of the embedded steel

The availability of oxygen and the moisture content at the steel surface are the two main factors determining the electrochemical potential of steel embedded in concrete, which is a very important parameter in relation to corrosion initiation. In order for pitting corrosion to occur the so-called equilibrium potential (E_{corr}) must be higher than the pitting potential (E_{pit}), i.e. $E_{corr} > E_{pit}$. The pitting potential is dependent on the concentration of chlorides and the presence of chlorides at the steel surface has the effect of changing E_{pit} to more negative

values. Consequently, higher contents of chlorides can be tolerated if the steel has a more negative potential.

For reinforcement in structures exposed to an atmospheric environment electrochemical potentials are typically found in the range between +100 mV and -200 mV vs. SCE [Bertolini, 2004], whereas the potential for reinforcement in submerged concrete structure usually have values around -400 to -500 mV vs. SCE. Higher chloride threshold values are thus expected for submerged concrete structures as compared to the ones under atmospheric exposure.

2.2.8 Surface condition of the steel

Several studies have demonstrated that the surface condition of the reinforcement has a significant influence on the chloride threshold value. In laboratory based investigations the steel may be subjected to a variety of different treatments before the testing is done. For example, the steel bars can be sandblasted, polished, chemically cleaned or pre-rusted, or the steel may be used “as-received”. Moreover, the surface of the steel bar can be either ribbed or smooth.

Mohammed and Hamada [2006] investigated the corrosion resistance of steel bars with various surface conditions (mill-scaled, polished, black- and brown-rusted, and bars that were covered with cement paste before casting (i.e. pre-passivated)). They reported that the chloride threshold value was highest for pre-passivated steel followed by gradually decreasing threshold values in the following order: black-rusted > polished > brown-rusted > mill-scaled. In a study on the corrosion behavior of different types of stainless steel Kouřil et al. [2010] found that the presence of scales on the steel surface leads to a significant decrease in corrosion resistance. Mammoliti et al. [1996] obtained higher chloride threshold values for polished steel surfaces as compared to ground or “as-received” samples, while Manera et al. [2007] found higher chloride threshold values for sandblasted steel bars as compared to steel bars with “as-received” surface conditions. Unfortunately, details regarding the conditions of the steel surface are often not reported in the literature, in spite of its strong influence on the chloride threshold value.

2.2.9 Condition of the steel-concrete interface

A dense layer of hydration products (containing a high proportion of Ca(OH)_2) is usually found at the interface between the reinforcing steel and the concrete [Page, 1975]. This layer can be of great importance for the chloride threshold value, since it has the ability to buffer the pH of the pore solution. At the same time, the dense layer of solid material may act as a physical barrier, which inhibits the charge transfer in certain areas, thus affecting the potential of the steel by limiting the area available for oxygen reduction [Page, 1975; Glass and Buenfeld, 1995].

Due to incomplete compaction or low workability of the concrete, macroscopic voids may be present at the steel-concrete interface, and Mohammed and Hamada [2001] have found that the direction of casting with respect to the orientation of the reinforcement affects the formation of voids. If the reinforcement is ribbed, it may also favor the formation of voids. The abovementioned dense layer may be weakened or absent in such voids, and Yonesawa et al. [1988] have reported that the chloride threshold value is significantly lower if the development of the dense layer at the steel-concrete interface is restricted. It has also been reported that the corrosion preferably occurs at the corners or indents of the profiling [Hansson and Sørensen, 1990]. In a recent study, Ann and Song [2007] found that the physical condition of the steel-concrete interface is more important for the chloride threshold value than the binding of chlorides or the buffering capacity of the cement paste matrix, especially the content of entrapped air voids was emphasized as being influential. Considering the importance of the conditions at steel-concrete interface for the chloride threshold value, it is unfortunate that these conditions are so difficult to quantify; it is very challenging to measure the volume of air-filled voids and other defects at the interface [Angst and Vennesland, 2007].

2.2.10 Method of chloride introduction

Reinforced concrete with cast-in chloride may be expected to have a different chloride threshold value in comparison with concrete exposed to chlorides from an external source [Nilsson et al., 1996]. This is due to a greater proportion of the chlorides being chemically bound to the hydration products, thus leading to a reduced concentration of free chlorides in the pore solution [Cavalier and Vassie, 1981].

2.2.11 Cracks

The presence of macrocracks (0.1 – 0.8 mm wide at the surface) in concrete can affect the chloride threshold value significantly [Pettersson et al., 1996], enhancing the transport rate of chloride. The effect of such macrocracks on the chloride threshold value is dependent on the size of the cracks, the exposure conditions and the cover thickness. Pettersson [1996] reported that the chloride threshold value was only marginally reduced for a submerged high performance concrete (30 mm cover thickness, water/binder ratio = 0.3, and 0.4 crack width) as compared with submerged, but uncracked, concrete. However, the chloride threshold value was reduced to almost zero when the same concrete (with cracks) was exposed to air.

3 Test methods

Generally, an experimental determination of the chloride threshold value for reinforced concrete must include the following four steps:

- A reinforcement bar (steel electrode) is embedded in a cement-based material, such as mortar or concrete, or immersed in a solution that simulates the concrete (synthetic pore solution/alkaline solution).
- Chlorides are introduced to the system. The chlorides can be added to the mix initially or introduced later by some kind of chloride exposure.
- Detection of corrosion initiation, for instance by measurement of potential shift or by visual inspection.
- Quantification of the chloride concentration at the time of corrosion onset. The concentration is determined as either total or free amount of chlorides, or as the $[\text{Cl}^-]/[\text{OH}^-]$ ratio.

As pointed out by Angst and Vennesland [2009], these four experimental steps offer a wide range of alternative routes, which can be chosen in order to reach a determination of the chloride threshold value. For example, when deciding which type of steel electrode to use for the experimental setup a variety of options exists: The steel bars can be smooth or ripped and they can be prepared in different ways (as-received, pre-rusted, polished, sand-blasted, etc.). Furthermore, a variety of steel types exist, such as normal carbon steel, galvanized steel and stainless steel.

The introduction of chlorides to the steel electrode also offers a number of alternative approaches. The type of chloride source must be select (typically NaCl or CaCl₂), and the chlorides can be introduced to hardened samples (cement paste, mortar or concrete) by either capillary suction and/or diffusion, or by some type of accelerated migration method. Alternatively, the chloride can be added initially during mixing of the paste/mortar/concrete. As for the detection of corrosion onset, numerous approaches exist (see Section 3.2). Lastly, the chloride content at the steel electrode can be determined (and expressed) in a variety of ways (see Section 3.1).

3.1 Methods for detecting or quantifying chloride in concrete

This section presents a selection of techniques that are commonly used for detecting or quantifying the content chloride in cement-based materials. A quantification of the chloride content at the depth of the reinforcement bar is the final step in an experimental determination of the chloride threshold value for the sample under investigation, and the chloride threshold value is usually expressed as either:

- Total chloride (by weight of cement/binder or by concrete).

- Free chloride (by weight of cement/binder or by concrete).
- Free chloride ion concentration (expressed as either mole/l or by the $[Cl^-]/[OH^-]$ ratio).

3.1.1 Colourimetric spray indicator (silver nitrate)

The presence of chloride in hardened concrete can be detected qualitatively by spraying a freshly broken concrete surface with a suitable indicator (typically 0.1N $AgNO_3$). This simple test method exists in different varieties, but generally the presence of chloride will be revealed by a change in colour [Bamforth et al., 1997]. The spray indicator test offers a rapid and practical method for visual examination of chloride penetration in hardened cement-based materials. However, this technique cannot be used to accurately quantify the content of chloride, but is merely applicable for obtaining a rough estimate of the chloride penetration depth.

3.1.2 Volhard titration [NT Build 208, 1984]

The NT Build 208 method [1984] can be used for determination of the total content of chloride in hardened concrete by dissolving a powdered concrete sample in a solution of nitric acid. Subsequently, the chloride content is determined by Volhard titration. The precision of the method is good provided that the sample contains about 2 g of cement and that the measurement is carried out by an experienced laboratory.

The total content of chloride in concrete is often assumed to be equal to the content of acid soluble chloride. However, Dhir et al. [1990] have demonstrated that it may represent only 90% of the total content of chloride due to incomplete dissolution.

3.1.3 Potentiometric titration

The total chloride content of hardened concrete can also be measured by potentiometric titration with silver nitrate by using a silver electrode, since the potential of an immersed silver electrode is a function of the concentration of silver ions in the solution. Initially, the powdered concrete sample is immersed in nitric acid in order to extract the chloride ions. This method offers a very good precision (if the operator is skilled and calibration is performed carefully).

3.1.4 Ion selective electrode

A chloride selective electrode embedded in concrete can be used to determine the content of free chloride in the pore solution. In essence, the activity of the chloride ions in solution is measured using e.g. a silver/silver chloride electrode. Investigations by Atkins et al. [1996] have demonstrated a good correlation between chloride concentrations obtained from ex-

tracted pore solutions with measured values from silver/silver chloride electrodes. However, the durability of the silver/silver chloride electrode has often been poor [magler reference].

3.1.5 X-Ray Fluorescence spectrometry

The total content of chloride in a concrete sample can be determined using X-Ray Fluorescence (XRF) spectrometry [Dhir et al., 1990]. Measurements are performed on pressed powder samples and the method does not require any acid digestion or extraction prior to analysis, but calibration standards with known content of chloride must be prepared [Building Research Establishment, 1977]. A drawback is the requirement of expensive equipment and a high level of expertise. Normally, the method is restricted to laboratories handling large numbers of samples.

3.1.6 Quantab chloride titrators

The total chloride content in a powdered concrete sample can be quantified using a so-called Quantab[®] chloride titrator, which consists of a thin, chemically inert plastic sheath. Laminated within the sheath is a strip impregnated with a reagent. When the Quantab[®] test strip is placed in a test solution, fluid rises up the strip by capillary action, and the reagent reacts with the chloride ion in the solution and produces a white column in the strip. The height of this column is proportional to the total chloride concentration. While this represents a convenient test method, Dhir et al. [1990] points out that the chloride content might be underestimated due to incomplete chloride extraction caused by an insufficient concentration of the nitric acid solution used in this test. Furthermore, the Quantab test method is limited to chloride concentrations in the range from 0.03% to 1.2% by weight of concrete.

3.1.7 Scanning electron microscopy

The total chloride content of hardened concrete can be determined using a scanning electron microscope provided that the microscope is equipped with an energy dispersive X-Ray (EDX) analyzer. The determination of the chloride concentration is based on the interaction between some X-ray source and the sample (polished thin section). However, this technique is expensive and requires extensive sample preparation as well as an operator with a high level of expertise.

3.1.8 Expression of pore solution

The pore solution of a concrete sample can be expressed, and subsequently collected for chemical analysis, by subjecting the sample of interest to a very high pressure. This method is often used to determine the amount of free chlorides in concrete [Ayra and Newman, 1990]. However, according to Glass et al. [1996] the pore pressing may also release loosely bound chlorides, thus overestimating the amount of free chlorides. Arya [1990] also pointed out that this technique involves some practical difficulties, especially when working with concrete samples having low water/cement ratios or containing coarse aggregate particles,

or if the samples are rather dry. Moreover, it is also important to note that the method gives an average value of the concrete volume under investigation, which may lead to inaccurate results in the case of high concentration gradients in the pore solution.

3.1.9 Leaching techniques

As an alternative to the expression of pore solution by pressure, the content of free chlorides may also be determined using a leaching technique. Several different varieties of the method have been used in the past using different solvents or different procedures with regard to leaching time and temperature. Generally, a crushed or powdered sample is mixed with a solvent and the amount of chloride passing into solution is subsequently measured. The most commonly used solvent is distilled water and the chloride concentration obtained from leaching methods is often referred to as water soluble chloride and is sometimes considered to be equal to free chloride.

Methanol and ethyl alcohol have also been used as alternative solvents. However, these are not very effective in leaching out the free chloride. The measured concentrations are up to 10 to 20 times lower when compared to the free chloride concentration found by pore solution expression [Tritthart, 1989; Arya et al., 1987]. The chloride concentrations obtained from the leaching techniques has also been found to be dependent on such factors as temperature and leaching time, and it has been demonstrated that the cement type and source of chloride (mixed-in or external) have to be known in order to select an accurate leaching procedure. Therefore, the technique is not very practical for determining the free chloride content [Arya, 1990].

Castelotte [2001] has presented a leaching technique to determine the amount of free chlorides of hardened cementitious materials. The principle is to extract the free chlorides by leaving the sample material in an alkaline solvent for 24 h. At a chloride content of 0.5% (by weight of sample) the method overestimated the free chloride content significantly, but at higher chloride contents the method corresponded better to results obtained from pore solution expression. It should be noted that rather high chloride concentrations have been used in this study, and it is uncertain if the method is also sufficiently accurate at lower and more “practical” chloride concentrations.

Leaching techniques are rarely used in Europe, whereas water soluble chloride analysis is used as a standard method [AASHTO T260-97, 2005] in North America.

3.2 Methods for determination of corrosion initiation

3.2.1 Potential shift (open circuit measurements)

The initiation of reinforcement corrosion in concrete can be detected by continuously measuring the potential of the steel bar under investigation. This is due to the fact that actively corroding steel has much more negative potentials than passive steel in concrete. The onset of corrosion is therefore indicated by a significant change in potential of the reinforcement steel [Hausmann, 1967; Gouda, 1970; Zimmermann, 2000]. Principally, this techniques measures the potential of the steel with respect to a standard reference electrode, e.g. saturated calomel electrode (SCE), copper/copper sulfate electrode (CSE) or silver/silver chloride electrode [Song and Sarawasthy, 2007]. Table 3.1 presents some probabilities of reinforcement corrosion according to the ASTM C 876 standard [1999]. However, it could be argued that this approach is too simple to be able to include varying exposure conditions, and it should probably only be used for concrete exposed in the atmospheric zone.

In an open circuit test setup the electrochemical potential of the steel electrode is very dependent on the oxygen availability, and the choice of exposure conditions (submerged, cyclic wetting, etc.) will greatly influence the chloride threshold value. Also, a notable limitation of the method is the lack of a universal correlation between corrosion rate and potential. For instance, for submerged concrete structures the oxygen availability can be significantly reduced and it is thus possible to measure potentials as low as -800 mV vs. CSE without occurrence of any corrosion [Bamforth et al., 1997] and a significant change in potential cannot be considered as a direct proof of corrosion initiation, since a potential drop also can be caused by other phenomena as well.

Table 3.1 Conditions of reinforcement corrosion related to open circuit potential measurements. [acc. to ASTM C 876]

Open circuit potential values		Corrosion condition
[mV vs. SCE]	[mV vs. CSE]	
< -426	<-500	Severe corrosion
<-276	< -350	High (<90% risk of corrosion)
-126 to -275	-350 to -200	Intermediate corrosion risk
> -125	> -200	Low (10% risk of corrosion)

3.2.2 Linear polarization resistance (LPR)

The instantaneous corrosion rate of a steel electrode can be determined by measuring the so-called linear polarization resistance [Bamforth et al., 1997; Angst and Vennesland, 2007]. The principle of the method is to apply a small current to the reinforcement in order to po-

larize it between 10 and 30 mV. This current is interrupted and the following response of the reinforcement potential is measured with time. The polarization curve is approximately linear near the corrosion potential, and the experimental measurement of the polarization curve in a small range around the equilibrium potential can yield the slope of the curve ($\Delta E/\Delta I$), which is defined as the polarization resistance R_p . The corrosion rate is finally obtained by employing the *Stern-Geary* equation:

$$i_{corr} = \frac{B}{R_p \cdot A}$$

where B is a constant that depends on the anodic and cathodic Tafel slopes and A is the polarized surface area on the reinforcement.

This technique is non-destructive and very fast, but in order to detect the initiation of active reinforcement corrosion, a significant corrosion rate has to be defined. A sustained current density of $0.1 \mu\text{A}/\text{cm}^2$ is generally accepted as the value above which the reinforcement is considered to be actively corroding [Andrade et al., 2004]. A downside of the technique is the required acquisition of rather advanced and expensive equipment.

3.2.3 Macrocell current

By connecting a steel electrode (reinforcement bar) to a counter electrode, a macrocell is formed and the current flow between those two electrodes can be monitored. Onset of reinforcement corrosion is indicated by a significant increase in current. Sometimes the working electrode (reinforcement bar) is polarized and held at a constant potential during the experiment (potentiostatic control) [Angst and Vennesland, 2007].

3.2.4 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) can be used to measure the corrosion rate of reinforcement in concrete. The technique is non-destructive and is generally suitable for studying electrochemical processes in inhomogeneous or multiphase materials. An alternating voltage of about 10 to 20 mV is applied to the reinforcement and the resulting current is measured for a range of frequencies [Song and Sarawathy, 2007]. The obtained electrochemical impedance spectra can be interpreted to give values such as the polarization resistance, which subsequently can be used to calculate the corrosion rate [Elsener and Böhni, 1986; Li and Sagüés, 2001]. Disadvantages of the technique include the requirement of expensive equipment, sophisticated software for data analysis as well as a skilled operator [Bamforth et al., 1997].

3.2.5 Galvanostatic pulse method

The galvanostatic pulse method [Elsener et al. 1994] is a rapid and non-destructive technique that can be used to measure the corrosion rate of reinforcement in concrete. The method relies on polarization resistance (R_p) measurements which are carried out by inducing a short anodic current pulse (50 μ A) into the reinforcement galvanostatically (= constant current) from a counter electrode placed on the concrete surface together with a reference electrode. The counter electrode measures the resulting transient anodic change of the reinforcement potential, and the results may be presented as a contour map of corrosion rate values. The galvanostatic pulse method can be performed using hand-held equipment.

3.2.6 Visual examination

Initiation of reinforcement corrosion can be identified by visual inspection of the steel surface if the reinforcement is removed physically from the concrete. Since the method is destructive and only can be performed once, the accuracy is inherently low: The amount of time that has passed between the actual corrosion onset and visual observation of rust on the steel surface is unknown [Angst and Vennesland, 2007]. The method has mostly been used in earlier works, but is also used today as a supplement to other techniques.

4 Chloride threshold values from the literature

A table of chloride threshold values from the literature is presented in Appendix 1. As mentioned earlier, the chloride threshold value for reinforcement in concrete can be expressed as either total content of chloride (% by weight of cement or concrete), content of free chloride (e.g. mole/l or % by weight of cement) or as the $[Cl^-]/[OH^-]$ ratio, and the reported threshold values in the Appendix 1 exhibit a wide scatter. The following ranges of chloride threshold values were found:

- Total chloride (% by weight of cement): 0.02 to 3.08.
- Free chloride: 0.045 to 3.22 (mole/l) or 0.07 to 1.16 % by weight of cement.
- $[Cl^-]/[OH^-]$ ratio: 0.01 to 20.

This pronounced variation of chloride threshold values originates not only from the influencing parameters presented in section 2.2, but also from the variety of different methods that have been employed to detect the initiation of reinforcement corrosion and to measure the content of chloride in the specimen of interest. It was generally not possible to narrow the broad ranges of reported chloride threshold values by dividing them into groups according to e.g. exposure environment, binder type, etc. An exception was the distinction between $[Cl^-]/[OH^-]$ ratios obtained using synthetic pore solutions versus values from experiments involving specimens of paste, mortar or concrete. There is a clear tendency of $[Cl^-]/[OH^-]$ ratios being lower if the experiments were performed in synthetic pore solutions (overall range: 0.01 – 4.9) as opposed to ratios derived from hardened samples (overall range: 0.05 – 20).

This difference is probably reflecting the notable effect that the condition of the steel-concrete interface has on the chloride threshold value. Finally, the table in Appendix 1 contains data from two studies [Castellote et al., 2002; Trejo and Pillai, 2003] in which chloride was introduced to mortar samples using a migration technique. The reported chloride threshold values from these studies stands out as being notably low with total chloride contents (by weight of cement) ranging from 0.02 to 0.24 and $[Cl^-]/[OH^-]$ ratios from 0.05 to 2.0.

A consensus seems to be lacking about which expression of the chloride threshold value is considered the most appropriate. Some researchers argue that the threshold value is best expressed as the content of free chloride, since only the free chloride ions are assumed to participate in the initiation of pitting corrosion. However, it has been pointed out that bound chlorides may be released due to, for example, a drop in pH of the pore solution [Glass et al., 2000; Reddy et al., 2002], and that the corrosion risk represented by the amount of bound chlorides is overlooked if only the free chlorides are taken into account [Glass and Buenfeld, 1997]. It should also be mentioned that contents of free chloride determined by expression of pore solution may not reflect the "true" content of free chloride in concrete at atmospheric pressure, since the expression method is carried out using a very high confining pressure, i.e. the conditions of phase equilibrium is most likely very different at such elevated pressures.

It is generally agreed that at the time of corrosion initiation it is the free chloride content which is relevant (considering all other parameters to be equal). However, for practical reasons measurements of free chloride content is very difficult to carry out, so it is often preferred to relate the chloride threshold value to the total chloride content. This introduces a problem which has generally not been taken into consideration so far, because the ratio between free and bound chloride can change considerably in different exposure situations (e.g. at different temperatures). The question is how can this be taken into account, when we measure the chloride threshold value in the lab?

The representation of the chloride threshold value by the $[Cl^-]/[OH^-]$ ratio relates the concentration of free chloride ions to the pH value of the pore solution. Again, it may be argued that this expression is associated with a problematic neglect of the bound chlorides. Furthermore, it has been demonstrated that the $[Cl^-]/[OH^-]$ threshold ratio depends on the pH value of the pore solution [Li and Sagüés, 2001]. The threshold ratio increases at higher pH values and consequently the actual pH value must also be taken into consideration when reporting the chloride threshold value by the $[Cl^-]/[OH^-]$ ratio.

It is also worth noting that the way one chooses to express the chloride threshold value may partly be a result of practical considerations. As noted above, it is far more difficult to measure the content of free chloride in a concrete specimen as compared to the total content of chloride. In the literature the majority of chloride threshold values are expressed by total content of chloride, which is possibly also a reflection of such practical concerns.

When comparing chloride threshold values reported in the literature it is important to keep in mind that the investigated specimens (concrete, mortar or cement paste) may not have reached the same degree of maturity at the time when they are exposed to a chloride-rich environment. The binder of a specimen in one study may have reacted almost completely, whereas the binder in another experiment may have reacted to a much lesser extent. For example, a number of studies have demonstrated that the fly ash component of a hydrating binder may react very slowly. Lam *et al.* [2000] found, using a selective dissolution method, that after 7 days of hydration only 6 % of the fly ash had reacted in pastes containing 45 – 55 wt% fly ash, and that more than 80 % of the fly ash still remained unreacted after 90 days of hydration. Feldman *et al.* [1990] have also reported that considerable amounts of fly ash remained as unreacted particles in the binder – fly ash pastes after 91 days of hydration. This was based on electron microscopy. Similarly, based on a solid-state NMR study on cement pastes containing 30% fly ash, Poulsen [2009] found that clear indications of fly ash reaction were only detected for hydration times beyond 28 days and that 75 – 80 % of the fly ash had still not reacted after 180 days of hydration. With such a slowly reacting component in the binder, the chemical composition (e.g. the pH value) of the pore solution will progressively change for an extended period of time thus affecting the chloride threshold value continuously. Therefore, the comparison of chloride threshold values from the literature may lead to ambiguous conclusions if the maturity of the specimen (at the time of chloride exposure) is not taken into consideration.

5 RILEM project

In order to address the lack of a universally accepted method for determination of the chloride threshold value in reinforced concrete a technical committee (TC 235 CTC: Corrosion Initiating Chloride Threshold Concentrations in Concrete) has been established under the RILEM organization. The committee comprises a group of experts that have been actively working within research areas related to chloride threshold values. The work of the committee was initiated in 2009 and has an estimated duration of four years. The primary aim is to develop a generally accepted test method for the determination of chloride threshold values for reinforced concrete and main activities of the committee include the preparation of a state-of-the-art report and the organization of round robin tests (RRTs).

After thorough discussions, the details of a preliminary test method have been agreed upon and a RRT was initiated during the autumn of 2011. The RRT involves 12 different laboratories and the main purpose is to evaluate the precision (repeatability and reproducibility) of the suggested test method for measuring the chloride threshold value in concrete. The method involves the exposure of concrete specimens (ten replicas) to a 3.3 mass% NaCl solution after initial subjection to a drying regime, which is done to facilitate a quicker ingress of chloride through the concrete. Each specimen contains an embedded steel bar (working electrode) and the potential of this working electrode against a reference electrode is moni-

tored by a data logger. The corrosion onset is detected by a significant drop in potential (at least 150 mV) and the chloride concentration at the steel bar is finally measured by potentiometric titration. In order to eliminate the possible influence of using different types of cement and steel, these materials have been distributed to all the participating laboratories, thus ensuring that the same materials are used by all laboratories. The obtained results from the RRT will be compared and discussed at RILEM workshops held in the period 2012-13.

6 Summary

Ingress of chloride ions into a concrete structure may lead to pitting corrosion on the reinforcement and ultimately result in deterioration of the structure. The corrosion process is initiated when a certain critical concentration of chloride (the chloride threshold value) is reached at the surface of the reinforcing steel. The chloride threshold value is a very important input parameter for the modeling of service lifetime of reinforced concrete structures and therefore, it is essential that the chloride threshold value can be experimentally determined in a reliable manner. Unfortunately, a generally accepted method for determination of chloride threshold values is presently lacking. Without an experimental determination, engineers are forced to make qualified (and often very conservative) guesses about the magnitude of the threshold value, thus potentially underestimating the service lifetime of concrete structures considerably.

It seems well-established that a “universal” chloride threshold value does not exist. Instead, the threshold value is dependent on a variety of factors, such as the type of binder used in the concrete mix, the electrochemical potential of the reinforcing steel, temperature, the surface condition of the steel, availability of oxygen, etc. As a consequence, the chloride threshold value must generally be considered as unique for each type of concrete and the associated environment to which the concrete is exposed.

The chloride threshold values reported in the literature display a wide scatter and have been obtained using a variety of different experimental approaches, thus making comparison of results questionable. Moreover, the chloride threshold value is generally reported using one of three different expressions (total content of chloride, content of free chloride, or $[Cl^-]/[OH^-]$ ratio of the pore solution), which further complicates the comparison of results.

In 2009 a technical committee was established as part of the RILEM association with the primary purpose of developing a new and generally accepted test method for determination of chloride threshold values in concrete. After careful discussions the committee has agreed upon a preliminary test method and the result from a Round Robin Test based on this new method are expected in the period 2012-13.

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Appendix 1: Chloride threshold values from the literature

Chloride threshold values reported by either total content of Cl^- (% by weight of cement), free content of Cl^- or by the $[\text{Cl}^-]/[\text{OH}^-]$ ratio. OPC = ordinary Portland cement; GGBS = ground granulated blast-furnace slag; LPR = linear polarization resistance; EIS = electrochemical impedance spectroscopy; FA = fly ash; SF silica fume; SRPC = sulphate resisting Portland cement; WE = working electrode; CE = counter electrode.

Total Cl^- (% cement wt)	Free Cl^-	$[\text{Cl}^-]/[\text{OH}^-]$	Composition of binder	Environment	Specimen	w/b	Chloride introduction	Condition of steel	Detection of corrosion onset	Reference
		0.5 – 1.08	-	laboratory, submerged	Alkaline solution	-	in solution	cleaned, smooth	potential, visual inspection	Hausmann [1967]
0.4			100% OPC	laboratory, 65% RH	mortar	0.45	mixed-in	smooth	visual inspection	Richartz [1969]
3.0			100% OPC	laboratory, exposed to air	concrete	0.6	mixed-in	smooth	anodic polarization, potential	Gouda and Halaka [1970]
1.0			35% GGBS + 65% OPC	laboratory, exposed to air	concrete	0.6	mixed-in	smooth	anodic polarization, potential	Gouda and Halaka [1970]
2.4			100% OPC	laboratory, submerged, but aerated	mortar suspension	-	mixed-in	smooth	anodic polarization, potential	Gouda and Halaka [1970]
1.2			35% GGBS + 65% OPC	Laboratory, submerged, but aerated	mortar suspension	-	mixed-in	smooth	anodic polarization, potential	Gouda and Halaka [1970]
0.2 – 1.4			various	outdoor exposure, exposed to air	various	-	mainly de-icing salts	-	potential	Stratfull et al. [1975]
0.4 – 0.8			100% OPC	laboratory, exposed to air	concrete	0.4	mixed-in	cleaned, ribbed	LPR	Locke and Siman [1980]
0.25 – 0.5			100% OPC	laboratory, submerged/ 60% RH	mortar	0.5	mixed-in	sandblasted	EIS, visual inspection	Elsener and Böhni [1986]
0.1 – 0.19			100% OPC	laboratory, exposed to air	concrete	0.45	mixed-in	polished	LPR, EIS, visual inspection, weight loss	Hope and Ip [1987]
0.1 – 0.19			100% OPC	outdoor exposure, exposed to air	concrete	0.45	mixed-in	polished	LPR, EIS, visual inspection, weight loss	Hope and Ip [1987]

Total Cl- (% cement wt)	Free Cl ⁻	[Cl ⁻]/[OH ⁻]	Composition of binder	Environment	Specimen	w/b	Chloride introduction	Condition of steel	Detection of corrosion onset	Reference
		4.9	100% OPC	laboratory, submerged, but aerated	synthetic pore solution	-	in solution	polished	LPR, potential	Yonezawa et al. [1988]
		0.25 – 0.8	-	laboratory, submerged	synthetic pore solution	-	in solution	cleaned	LPR, potential	Goñi and Andrade [1990]
0.4 – 1.37			OPC, FA, SRPC, SF, RHPC	laboratory, submerged	mortar	0.4 – 0.6	diffusion	cleaned, smooth	current between WE and passive external CE	Hansson and Sørensen [1990]
0.5				laboratory, exposed to air	concrete	0.4 – 0.6	mixed-in	-	macrocell current	Schiessel and Raupach [1990]
0.5 – 2.0				laboratory, exposed to air	concrete	0.4 – 0.6	mixed in/ diffusion/capillary suction	-	macrocell current	Schiessel and Raupach [1990]
1.5 – 2.5		3 – 20	OPC, SRPC	laboratory, exposed to air	Cement paste/ concrete	0.5	capillary suction and diffusion/mixed-in	cleaned, smooth	LPR, potential	Lambert et al. [1991]
0.125			70% OPC + 30% SF	laboratory, submerged	concrete	-	diffusion	-	half-cell potential	Takagi et al. [1991]
0.5 – 1.8	0.36 – 3.22 mole/l		OPC, SF, FA	laboratory, exposed to air	mortar	0.4 – 0.6	capillary suction and diffusion/mixed-in	cleaned	LPR	Pettersson [1992]
	0.14 – 1.8 mole/l	2.5 – 6	OPC, SF	laboratory, exposed to air	mortar and concrete	0.3 – 0.75	diffusion/capillary suction	ribbed	LPR	Pettersson [1995]
	0.14 mole/l		-	laboratory, submerged	alkaline solution	-	in solution	ground	anodic polarization	Mammoliti et al. [1996]
	0.28 mole/l		-	laboratory, submerged	alkaline solution	-	in solution	ribbed	anodic polarization	Mammoliti et al. [1996]
	0.42 mole/l		-	laboratory, submerged	alkaline solutions	-	in solution	polished	anodic polarization	Mammoliti et al. [1996]
0.5 – 1.0			100% OPC	laboratory, exposed to air	concrete	0.5 – 0.7	mixed-in/diffusion	ribbed	macrocell current	Schiessl and Breit [1996]

Total Cl- (% cement wt)	Free Cl ⁻	[Cl ⁻]/[OH ⁻]	Composition of binder	Environment	Specimen	w/b	Chloride introduction	Condition of steel	Detection of corrosion onset	Reference
1.0 – 1.5			OPC with GGBS or FA	laboratory, exposed to air	concrete	0.5 – 0.7	mixed-in/diffusion	ribbed	macrocell current	Schiessl and Breit [1996]
0.2 – 0.65			OPC with 15% to 50% FA	outdoor exposure, tidal zone (marine exposure)	concrete	0.32 – 0.68	capillary suction and diffusion	ribbed	weight loss	Thomas et al. [1996]
	0.44 – 0.65 mole/l		100% OPC	laboratory, submerged	mortar	0.75	capillary suction and diffusion	not reported	potential	Elsener et al. [1997]
	0.056 mole/l	0.26	-	laboratory, submerged	synthetic pore solution	-	in solution	cleaned	potentiostatic control	Breit [1998]
0.25 – 0.75			100% OPC, 100% SRPC and OPC with SF, FA or GGBS.	laboratory, submerged	mortar	0.5 – 0.6	diffusion	smooth	potentiostatic control, visual inspection	Breit [1998]
0.4 – 1.5			100% SRPC or SRPC with FA, SF and GGBS	outdoor exposure (seawater)	concrete	0.3 – 0.75	diffusion	ribbed, as received	potential, LPR, galvanostatic pulse	Sandberg [1998]
1.24 – 3.08	0.39 – 1.16 % cem wt	1.17 – 3.98	100% OPC	laboratory, 100% RH	mortar	0.5	mixed-in	ribbed and smooth	LPR, potential	Alonso et al. [2000]
		0.7 – 1.7	-	laboratory, oxygen supply	Synthetic pore solution	-	in solution	sandblasted, cleaned	potential, macro-cell current	Zimmermann et al. [2000]
0.25 – 1.25	0.045 – 0.55 mole/l		100% OPC	laboratory, exposed to air	mortar	0.6	capillary suction/diffusion	sandblasted, cleaned	potential, macro-cell current	Zimmermann et al. [2000]
0.2 – 0.4			100% OPC	outdoor exposure	concrete	-	diffusion	-	macrocell current	Zimmermann [2000]
		0.01 – 2.5	-	laboratory, submerged	alkaline solutions	-	in solution	as received, sandblasted, pre-rusted	Potential, EIS	Li and Sagüés [2001]
0.73	0.50 % cem wt	1.76±0.3	OPC, SRPC, FA	laboratory submerged	mortar	0.5	diffusion	ribbed, millscaled	Potentiostatic control	Alonso et al. [2002]
0.23	0.36 mole/l	1.5	100% SRPC	laboratory, exposed to air	mortar	0.37	diffusion	ribbed	LPR, potential	Castellote et al. [2002]

Total Cl- (% cement wt)	Free Cl ⁻	[Cl ⁻]/[OH ⁻]	Composition of binder	Environment	Specimen	w/b	Chloride introduction	Condition of steel	Detection of corrosion onset	Reference
0.15	0.33 mole/l	2.0	100% SRPC	laboratory, exposed to air	mortar	0.37	migration	ribbed	LPR, potential	Castellote et al. [2002]
~0.4			100% OPC (~7 and ~12% C ₃ A)	laboratory, exposed to air (23°C, 50% RH)	concrete	0.4 – 0.6	mixed-in	cleaned (acetone)	potentiostatic testing, visual inspection	Whiting et al. [2002]
~0.4			75% OPC + 25% FA (Class C and F)	laboratory, exposed to air (23°C, 50% RH)	concrete	0.4 – 0.6	mixed-in	cleaned (acetone)	potentiostatic testing, visual inspection	Whiting et al. [2002]
0.02 – 0.24		0.05 – 0.62	100% OPC	laboratory, submerged	mortar	0.5	migration	cleaned	LPR	Trejo and Pillai [2003]
0.68 – 0.97	0.07 – 0.13 % cem wt	0.16 – 0.26	OPC with 15 to 30% FA or 30% GGBS	laboratory, exposed to air	concrete	0.35 – 0.55	mixed-in	smooth	potential	Oh et al. [2003]
0.45	0.10 % cem wt	0.27	SRPC	laboratory, exposed to air	concrete	0.35 – 0.55	mixed-in	smooth	potential	Oh et al. [2003]
0.52 – 0.75			100% OPC	laboratory, exposed to air (22% RH and 30 °C for 60 days) then submerged	concrete	0.45	Capillary suction and diffusion	smooth	potentiostatic control	Nygaard and Geiker [2005]
	0.4 – 0.8 % cem wt (water-soluble)		100% OPC	laboratory, exposed to air	concrete	0.5	capillary suction and diffusion	polished, rusted, millscaled	LPR, potential, visual inspection	Mohammed and Hamada [2006]
1.1 – 2.0			100% OPC	laboratory, exposed to air	concrete	0.60	mixed-in	smooth, ribbed, as received and sandblasted	LPR, potential	Manera et al. [2007]
0.6 – 1.2			90% OPC + 10% SF	laboratory, exposed to air	concrete	0.60	mixed-in	smooth, ribbed, as received and sandblasted	LPR, potential	Manera et al. [2007]