Cement and Concrete Research 39 (2009) 1122–1138

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Critical chloride content in reinforced concrete — A review

Ueli Angst [a,*], Bernhard Elsener [b], Claus K. Larsen [a,c], Øystein Vennesland [a]

[a] *NTNU Norwegian University of Science and Technology, Department of Structural Engineering, Richard Birkelandsvei 1A, N-7491 Trondheim, Norway*
[b] *ETH Zurich, Institute for Building Materials (IfB), ETH Hönggerberg, CH-8093 Zurich, Switzerland*
[c] *Norwegian Public Roads Administration, N-0033 Oslo, Norway*

ARTICLE INFO

Article history:
Received 15 October 2008
Accepted 13 August 2009

Keywords:
Corrosion
Durability
Chloride
Reinforcement

ABSTRACT

Chloride induced corrosion as the major cause for degradation of reinforced concrete has been the subject of great research efforts over the last fifty years. The present literature review summarises the state of the art by presenting the concept of the critical chloride content, discussing influencing factors, and assessing available measurement techniques. A large number of published chloride threshold values together with the respective experimental details are collected. While today's experience is mostly based on Portland cement, more modern studies with non-traditional binders often reported contradictory results. The present literature evaluation highlights the strong need for a practice-related test method, and, in this regard, focuses especially on experimental procedures by discussing advantages and drawbacks of methods and setups. It clearly emerges that many of the setups used to determine critical chloride contents are not suited to give realistic results.

Contents

---

* Corresponding author. Tel.: +47 735 94 538.
E-mail address: ueli.angst@ntnu.no (U. Angst).

0008-8846/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2009.08.006

1. Introduction

After it was recognised in the second half of the last century that chloride may induce steel corrosion in reinforced concrete structures, great research efforts have been made in this regard: over the last fifty years, a considerable amount of papers has been published presenting values for critical chloride content (C_{crit}) in reinforced concrete [1–53]. Considering marine exposure conditions and the extensive use of de-icing salts in many countries, chloride induced corrosion is one of the most common causes of degradation of reinforced concrete structures. Both for the design of new structures and for condition assessment of existing structures, knowledge of reliable C_{crit} values is important as the remaining service life is often considered as the time required to reach the chloride threshold value at the depth of the reinforcement. In probabilistic service life modelling, C_{crit} has been identified to be one of the most decisive input parameters [54,55].

Despite the multitude of studies undertaken, many aspects of chloride induced reinforcement corrosion in concrete are still incompletely understood and no general agreement on a C_{crit} value has been achieved. Results reported in the literature scatter over a large range [56–58]. This is not only the result of different definitions, measuring techniques and testing conditions, but also owing to the stochastic nature and complexity of initiation of pitting corrosion. Thus, often conservative values are nowadays used as critical chloride content: In European countries as well as in North America it has become common practice to limit the tolerable chloride content to or around 0.4% by weight of cement [59]. In probabilistic modelling the critical chloride content is a stochastic variable as e.g. in the fib *model code for service life design* [60], where C_{crit} is 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. Although there is a strong need for reliable C_{crit} values, an accepted or standardised test method to measure critical chloride does at present not exist.

The present review summarises the state of the art regarding critical chloride content in reinforced concrete. It is not only aimed at collecting C_{crit} values reported in the literature, but also all the relevant details about experimental procedures are collated. The data is analysed with regard to factors that have an influence on C_{crit}, thereby focussing on experimental setups and measurement techniques. By highlighting advantages and drawbacks of experimental parameters, a basis for developing a test setup will be provided. In addition, the literature evaluation will reveal certain aspects of chloride induced reinforcement corrosion in concrete, that are currently not well understood and where researchers working in this field need to focus on.

Only carbon steel is considered, although a limited number of publications on corrosion resistant reinforcement in connection with critical chloride content can be found in the literature, e.g. [19,61–63]. Minor parts of this review were presented in [64].

2. Concept of critical chloride content

2.1. Definitions

Reinforcement corrosion in non-carbonated, alkaline concrete can only start once the chloride content at the steel surface has reached a certain threshold value [65]. In the literature, this value is often referred to as *critical chloride content* or *chloride threshold value*. In the present work, both terms — or simply the abbreviation C_{crit} — are used.

Two different ways of defining C_{crit} are common [22,66]: From a scientific point of view, the critical chloride content can be defined as the chloride content required for depassivation of the steel (Definition 1), whereas from a practical engineering point of view C_{crit} is usually the chloride content associated with visible or "acceptable" deterioration of the reinforced concrete structure (Definition 2).

It has to be emphasized that the two definitions are related to different phenomena: the depassivation-criterion in Definition 1 only considers the initiation stage, whereas in the case of Definition 2 with visible or acceptable deterioration as a criterion, also the propagation stage is included. As a result, the two definitions lead to different C_{crit} values. Fig. 1 illustrates this by combining Tuutti's corrosion model [67] with an assumed curve representing the chloride concentration at the steel reinforcement vs. time. The figure clearly shows that using the practical definition leads to higher C_{crit} values. It is important to understand that this is only the result of a longer time passing until the chloride content is determined. The rate at which corrosion proceeds has a large influence on when this is done and thus greatly affects the chloride threshold value when applying this definition.

Definition 1 is more precise, since it expresses the chloride content that is directly related to depassivation. In Definition 2, the chloride

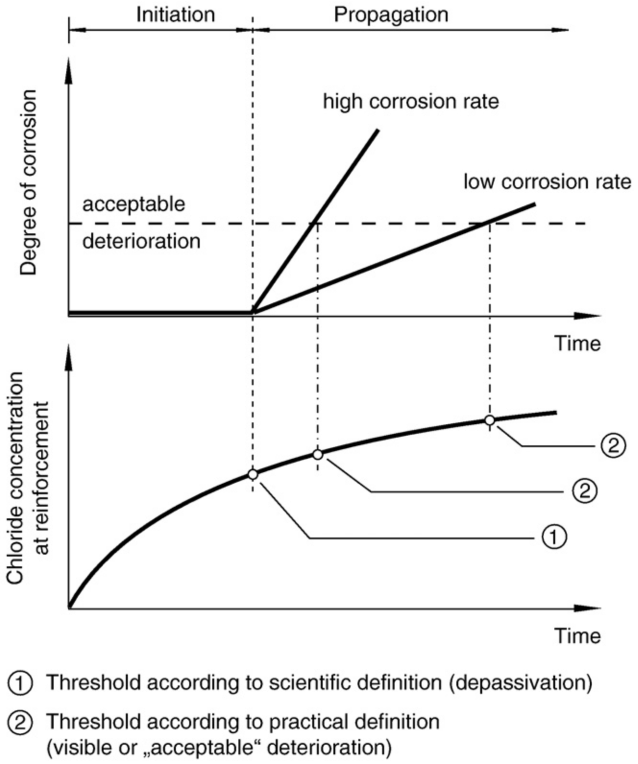

Fig. 1. Definitions for chloride thresholds (based on Tuutti's model [67]).

Table 1
Possibilities to express the critical chloride content.

Aggressive species	Inhibitive property	Expressed as
Total chloride	Weight of cement/binder	% by weight
	Weight of concrete	% by weight
	Acid neutralisation capacity	$(Cl^-)/(H^+)$ mole ratio
Free chloride	Weight of cement/binder	% by weight
	Weight of concrete	% by weight
Free chloride ion concentration	–	mol/l
	OH^- concentration	$(Cl^-)/(OH^-)$ mole ratio

content associated with an acceptable degree of corrosion has no theoretical background: the amount of chloride that is measured at that time has nothing to do with the degree of corrosion or the corrosion rate. Also the term “acceptable degree” is imprecise and thus Definition 2 results in a larger scatter of C_{crit} values. In the literature, these two definitions are often mixed up. Care has thus to be taken when comparing and evaluating results reported by different researchers.

2.2. Expression of C_{crit}

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 measurement of total chloride content is relatively simple and well documented in standards [68,69]. Since the quantification of the binder content in hardened concrete can be difficult, it is sometimes preferred to express C_{crit} as *total chloride content relative to the weight of the concrete*.

By assuming that the bound chlorides are completely removed from the pore solution and present no risk for pitting initiation, it would make sense to only consider the free chlorides. Thus, chloride threshold values are also expressed by the use of *free chloride contents*, either related to the weight of cement or concrete or as concentration in the pore solution.

Another commonly used form to express critical chloride thresholds relates the chloride ion activity to the pH of the pore solution, i.e. C_{crit} is presented in terms of $(Cl^-)/(OH^-)$ or just Cl^-/OH^-. Publications often cited in this regard are those by Hausmann [6] and Gouda [8], but chloride threshold values in terms of Cl^-/OH^- have

Table 2
Published C_{crit} values under outdoor exposure conditions or from real structures.

C_{crit}	Experimental details							Year	Reference
Total Cl^- (%bw)	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Corrosion detection	C_{crit} def.		
0.2 – 1.4[a]	(Na)	CAP + DIF	C (NR)	NR	NR (RIB; AR)	E	1–2	1975	Stratfull et al. [10]
0.25 – 1.5	(Na)	CAP + DIF	C (NR)	NR	NR (RIB; AR)	E	1–2	1984	Vassie [12]
0.1 – 0.19	Ca, (Na)	MIX	C (0.45)	OPC	P	LPR, EIS, VI, WL	1	1987	Hope and Ip [16]
0.96 – 1.96	Ca	MIX	C (0.6, 0.75)	OPC	SB, CL	WL	2	1989	Treadaway et al. [19]
0.7	Seawater	CAP + DIF	C (0.32… 0.68)	OPC	NR	WL	1–2	1996	Thomas et al. [23,31]
0.2 – 0.65	"	"	"	FA	"	"	"	"	"
0.4 – 1.5	Seawater	DIF	C (0.3… 0.75)	SRCP, FA, SF, GGBS	RIB; AR	E, (LPR, GP)	1–2	1998	Sandberg [36]
0.2 – 0.4	Na	DIF	C (NR)	NR	NR	MC	1	2000	Zimmermann [39]
0.72	Seawater	CAP + DIF	C (NR)	NR	NR (RIB; AR)	VI	1–2	2001	Fluge [41]
0.4 – 1.3	Na	MIX, CAP, DIF	C (0.4, 0.6)	OPC	NR	LPR, E	1	2004	Morris et al. [45,48]
0.1 – 1.96									min… max

Table 3
Published C_{crit} values obtained from experiments with the steel directly immersed in solution (laboratory conditions).

C_{crit}		Experimental details				Year	Reference
Free Cl^- (mol/l)	Cl^-/OH^-	Chloride cation	Steel condition	Corrosion detection	Remarks		
0.17–0.34		Na	NR	E	In “cement extract”	1955	Bird, presented in [3]
	0.02–0.13	Na	ABR, CL	GP	Solution aerated, pH 12.6	1962	Rajagopalan et al. [4]
	1.0	Na	ABR, CL	GP	Solution stirred with nitrogen, pH 13	1965	Venu et al. [5]
	0.6	Na	SM, P, CL	E, (VI)	Solution aerated pH 11.6–13.2	1967	Hausmann [6]
	0.57	Na	SM, P, CL	GP, E, (VI)	pH 11.8	1970	Gouda [8], Diamond [14][a]
	0.48	"	"	"	pH 12.1	"	"
	0.29	"	"	"	pH 12.6	"	"
	0.27	"	"	"	pH 13.0	"	"
	0.30	"	"	"	pH 13.3	"	"
0.6%[b]		Na	SM, P, CL	GP	OPS mortar suspension	1970	Gouda and Halaka [9]
0.3%[b]		"	"	"	GGBS mortar suspension	"	"
	4.9	Na	P	LPR, E	Solution aerated, pH 13.8	1988	Yonezawa et al. [18]
	0.25–0.8	Na, Ca	P, CL	LPR, E	pH 11.64–13.22	1990	Goñi and Andrade [20]
0.14		Na	ABR, CL	PDP	Sat. $Ca(OH)_2$	1996	Mammoliti et al. [29]
0.28		"	RIB, CL	"	"	"	"
0.42		"	P	"	"	"	"
0.056	0.26	Na	CL	PC	pH 13.5	1998	Breit [34]
	0.7–1.7	Na	SB; CL	E, MC	Solution aerated, pH 13.2–13.5	2000	Zimmermann et al. [37,39]
	0.01–0.04	Na	AR (MIL); SB; PR	E, EIS	pH 12.6	2001	Li and Sagüés [40]
	0.2–0.8	"	"	"	pH 13.3	"	"
	1.0–2.5	"	"	"	pH 13.6	"	"
0.0056	0.178	Na	CL	PDP	pH 12.5	2004	Moreno et al. [49]
0.28	0.313	"	"	"	pH 13.9	"	"
0.0056–0.42	0.01–4.9						min… max

[a] Diamond evaluated the results by Gouda, that did not report specific C_{crit} values, but a linear relationship between pH and the logarithm of the chloride concentration.

[b] It is not clearly stated in the article whether this percentage is related to the sample weight, cement weight or water in the mix.

Table 4
Published C_{crit} values obtained from experiments with the steel embedded in cement based material (laboratory conditions).

C_{crit}			Experimental details							Year	Reference
Total Cl^- (%bw)	Free Cl^-	Cl^-/OH^-	Chloride cation	Chloride introduction	Specimen (w/b)	Cement type	Steel condition	Corrosion detection	Remarks		
0.32			Ca	MIX	C (NR)	NR	ABR, CL	GDP, VI	Submerged	1959	Kaesche [1]
0.57–1.09			Ca, Al	MIX	C (0.7)	NR	NR	PDP, VI	Submerged	1959	Bäumel [2]
>0.4			Ca	MIX	M (0.45)	OPC	SM	VI	No corrosion observed	1969	Richartz [7]
0.45%[a]			Na	MIX	C (0.6)	OPC	SM; P, CL	GP		1970	Gouda and Halaka [9]
0.15%[a]			"	"	"	GGBS	"	"		"	"
0.4–0.8			Na	MIX	C (0.4)	OPC	RIB; CL	LPR, (GDP)	Exposure to air	1980	Locke and Siman [11]
0.25–0.5			Ca	MIX	M (0.5)	OPC	SB	EIS, VI	Submerged/ 60% RH	1986	Elsener and Böhni [13]
		>0.69	Na, Ca	MIX	CEP	OPC	ABR, CL	LPR		1986	Andrade and Page [15]
		>0.31	"	"	"	GGBS	"	"		"	"
0.1–0.19			Ca, (Na)	MIX	C (0.45)	OPC	P	LPR, EIS, VI, WL	Wet/dry cycles	1987	Hope and Ip [16]
		7–45	Na	MIX, DIF	M (0.5)	OPC	P	LPR, E	Submerged (but aerated)	1988	Yonezawa et al. [18]
0.2–0.68			Na, (Ca)	DIF	M (0.4… 0.6)	OPC, FA, SF, SRPC, RHPC	SM, (RIB); CL	PC, E, LPR	PC at 0 V SCE	1990	Hansson and Sørensen [21]
0.48–2.02			NR	MIX, CAP + DIF	C (0.4… 0.6)	OPC, FA, SF, GGBS, SRPC	NR	MC	Macro-cell	1990	Schiessl and Raupach [22]
1.5–2.5		3–20	Na	CAP + DIF	CEP, C (0.5)	OPC, SRPC	SM; SB, CL	LPR, E, WL		1991	Lambert, Page et al. [24,25]
0.4–2.0			"	MIX	"	"	"	"	"	"	"
0.5–1.8	0.36–3.22 mol/l		Na	CAP + DIF, MIX	M (0.4… 0.6)	OPC, SF, FA	CL	LPR	Exposure to air	1992	Pettersson [26]
	0.14–1.83 mol/l	2.5–6	Na	CAP + DIF, MIX	M, C (0.3… 0.75)	OPC, SF	RIB	LPR	Exposure to air	1995	Pettersson [27]
0.5–1.0			Na	MIX, DIF	C (0.5… 0.7)	OPC	SM	MC	Exposure to air	1996	Schiessl and Breit [30]
1.0–1.5			"	"	"	GGBS, FA	"	"	"	"	"
	0.44–0.65 mol/l		Na	CAP + DIF	M (0.75)	OPC	NR	E		1997	Elsener et al. [32]
0.25–0.75	0.1 mol/l		Na	DIF	M (0.5… 0.6)	OPC, SF, FA, SRPC, GGBS	SM	PC, VI	Submerged	1998	Breit [35]
1.24–3.08	0.39–1.16%bw	1.17–3.98	Na, (Ca)	MIX	M (0.5)	OPC	RIB, SM	LPR, E	100% RH	2000	Alonso et al. [38]
0.25–1.25	0.045–0.55 mol/l		Na	CAP + DIF	M (0.6)	OPC	NR	E, MC		2000	Zimmermann et al. [37,39]
0.735	0.51%bw	1.67 ± 0.3	Na	CAP + DIF	M (0.5)	OPC, SRPC, FA	RIB; MIL	PC	$E > -0.2$ V SCE	2002	Alonso et al. [43]
1.0–8.34	1.0–4.0%bw	1.7–20	"	"	"	"	"	"	$E < -0.2$ V SCE	"	"
0.62	0.36 mol/l	1.5	Na	CAP + DIF	M (0.37)	SRPC	RIB	LPR, E	95% RH	2002	Castellote et al. [42]
0.42	0.33 mol/l	2.0	"	MIG	"	"	"	"	"	"	"
	0.4%bw		Na	CAP + DIF	M (0.58)	OPC, FA, SF	NR	LPR, E	Exposure to air	2002	de Rincón et al. [44]
0.04–0.24		0.09–0.62	NR	MIG	M (0.5)	OPC	CL	LPR	Submerged	2003	Trejo and Pillai [46]
0.68–0.97	0.07–0.13%bw	0.16–0.26	Na	MIX	C (0.35… 0.55)	OPC, FA, GGBS	(SM)	E, VI	95% RH	2003	Oh et al. [47]
0.45	0.10%bw	0.27	"	"	"	SRPC	"	"	"	"	"
0.4–1.3			Na, seawater	MIX, CAP + DIF	C (0.4, 0.6)	OPC	NR	LPR, E	Submerged; exposure to air	2004	Morris et al. [45,48]
0.52–0.75			Na	CAP + DIF	C (0.45)	OPC	SM	PC	PC at 0 V SCE	2005	Nygaard and Geiker [50]
0.05–0.15			NR	MIG	M (0.5)	OPC	MIL	LPR	Submerged	2005	Trejo and Monteiro [51]
	0.4–0.8%bw		Seawater	CAP + DIF	C (0.5)	OPC	P, PR, MIL, PP	LPR, E, PDP, VI	Exposure to air	2006	Mohammed and Hamada [52]
1.1–2.0			Na	MIX	C (0.6)	OPC	SM, RIB; AR, SB	LPR, E	Exposure to air	2008	Manera et al. [53]
0.6–1.2			"	"	"	SF	"	"	"	"	"
0.04–8.34	0.045–3.22 mol/l 0.07–1.16%bw	0.09–45									min… max

[a] It is not clearly stated in the article whether this percentage is related to the sample weight, cement weight or water in the mix.

already been mentioned earlier, e.g. by Venu et al. [5]. Whereas Hausmann [6] suggested a constant value for the Cl^-/OH^- ratio, Gouda [8] found a linear relation between pH and the logarithm of the chloride concentration with a slope of 0.83, which yields that the ratio $(Cl^-)^{0.83}/(OH^-)$ is a constant. This relation implies that the inhibiting effect of the hydroxide ions becomes stronger with increasing pH. Li and Sagüés [40] also reported that the Cl^-/OH^- threshold ratio increases with higher pH.

Although Cl^-/OH^- threshold ratios are apparently not constant values, this form is often considered as the most accurate way to express critical chloride contents. Glass and Buenfeld [70], however, argue that this is not supported by analysis of available data in literature. From their analysis of reported C_{crit} values it was concluded that presenting critical chloride thresholds is best done in the form of total chloride by weight of cement. They mainly argued that the inhibitive properties of the concrete cannot be expressed only by the OH^- concentration in the pore solution, since also a lot of other factors such as the alkaline reserves of the concrete (buffer capacity) and the condition of the steel–concrete interface affect C_{crit}. Moreover, they point out that if only the free chlorides are taken into account, the corrosion risk presented by bound chlorides — which might be released as a consequence of several factors — is ignored.

Also Page and Havdahl [71] wrote that the Cl^-/OH^- ratio is not a reliable index. In connection with experiments involving silica fume they found that addition of silica fume increases the Cl^-/OH^- ratio in the pore solution (as a result of less chloride binding and a lower pH). On the other hand, it also leads to a denser microstructure, which not only slows down chloride ingress, but also reduces the oxygen content and thus depresses the steel potential. These effects might compensate for the negative effects on the pore solution chemistry, and thus a higher Cl^-/OH^- ratio in the pore solution must not necessarily be accompanied by a higher risk of corrosion initiation.

Glass et al. proposed to express C_{crit} as the total chloride content relative to the resistance presented by the concrete to a fall in pH (acid neutralisation capacity) [70,72,73]. The amount of acid (moles of H^+) required to reduce the pH of suspensions of ground concrete samples to a certain value is thereby used to quantify the buffer capacity of the concrete and represents its inhibitive properties. Published critical chloride contents for various binder types have been evaluated with regard to this, and rather consistent values for C_{crit} have been found: in terms of the ratio of total chlorides (moles of acid soluble chloride) to the acid neutralisation capacity (moles of H^+), simply written as Cl^-/H^+, the same value of ca. 0.01 has been obtained for all binder types considered [72]. Whereas this method of expressing and determining C_{crit} values still needs further research, it might be promising in the sense that it includes both free and bound chlorides as the aggressive species and relates them to a decisive property of the hydration products.

From a practical point of view, it is important to bear in mind that it is difficult or even impossible to measure the free chloride content or the pH of the concrete pore solution. Accurate values are thus often unknown. It is comparatively simple to determine the total chloride and to relate it to the weight of concrete or cement.

Table 1 sums up the main forms of expression of chloride contents in concrete and shows how they reflect the aggressive species and inhibitive properties of the concrete.

3. Critical chloride contents in the literature

Numerous publications in connection with C_{crit} can be found in the literature. Occasionally, C_{crit} values have also been reported based on calculations and results from others: For example in Refs. [17,28], the authors determined the pH after pore liquid expression, and used Cl^-/OH^- ratios according to Hausmann [6] and Gouda [8] to estimate the tolerable chloride concentration in the pore solution; a method to detect depassivation, however, was not included in the experiments and thus the results provide no new findings with regard to the chloride threshold. In Ref. [74], on the other hand, depassivation was experimentally detected, but the corresponding chloride content was estimated with a theoretical diffusion model and not determined experimentally. Results of such studies are not considered in the present literature evaluation, since the experimental setups are not complete.

With reference to critical chloride content, also standards and regulations are occasionally cited, as they often present limits on the tolerable chloride content in concrete, for instance the European standard EN 206-1 that restricts the chloride content to 0.2… 0.4% chloride by mass of binder for reinforced concrete and 0.1… 0.2% for prestressed concrete [75]. These limits, however, are not proper chloride threshold values, but rather practical guidelines for the production of fresh concrete.

Tables 2–4 summarise all the publications considered in the present evaluation. Since these C_{crit} values were obtained from a variety of experimental setups, the corresponding details have to be considered when comparing them. The regarding information is also given in Tables 2–4, with abbreviations according to Table 5. For results from field studies (Table 2) it is not always clear whether the corrosion state is close to depassivation or corresponds to a later stage in the propagation period; the numbers given in column 8 indicate which definition (according to Section 2.1) is more likely to be true. The reported C_{crit} values in Table 2 are derived from investigations of bridge decks and coastal structures [10,12,39,41] or samples under outdoor exposure conditions [16,19,31,36,48]. In the case of laboratory studies, both with the steel directly immersed in alkaline solutions (Table 3) and when embedded in a cement based material (Table 4), corrosion was mostly detected close to depassivation due to the application of electrochemical techniques, and thus the values correspond more to Definition 1 (an exception from this is the work by Richartz [7]). In some publications [7,15,76] only lower boundaries for C_{crit} were reported, since no corrosion activity was detected at the time of measurement of chloride content.

Figs. 2 and 3 show reported C_{crit} values expressed in the form of total chloride by binder weight and in terms of Cl^-/OH^- ratios, respectively. Also these diagrams summarise relevant experimental data. Together with Tables 2–4 they will be the basis for the detailed literature evaluation in the following sections.

From a global perspective, a large overall scatter is apparent: The reported values range from 0.04 to 8.34% total chloride by weight of cement and by this over two orders of magnitude; in terms of Cl^-/OH^- ratios even from 0.01 to 45 and by this over three orders of

Table 5
Abbreviations used in Tables 2–4 and Figs. 2, 3, and 6.

Abbreviation	Meaning
CAP	Chloride introduced by capillary suction
DIF	… diffusion
MIG	… migration
MIX	… Added to the mix
C	Concrete
M	Mortar
CEP	Cement paste
OPC	Ordinary Portland cement
FA	Fly ash
SF	Silica fume
GGBS	Ground granulated blast furnace slag
SRPC	Sulphate resistant Portland cement
RHPC	Rapid hardening Portland cement
RIB	Ribbed steel bars
SM	Smooth steel bars
SB	Sandblasted
ABR	Abraded
P	Polished
AR	As-received
MIL	Mill-scaled
PR	Pre-rusted
PP	Pre-passivated
CL	Cleaned/degreased
LPR	Linear polarisation resistance
E	Potential
EIS	Electrochemical impedance spectroscopy
MC	Macro-cell current
WL	Weight loss
PC	Potentiostatic control/polarisation
GP	Galvanostatic polarisation
PDP	Potentiodynamic polarisation
GDP	Galvanodynamic polarisation
VI	Visual inspection
NR	Not reported
%bw	Total chloride by weight of binder

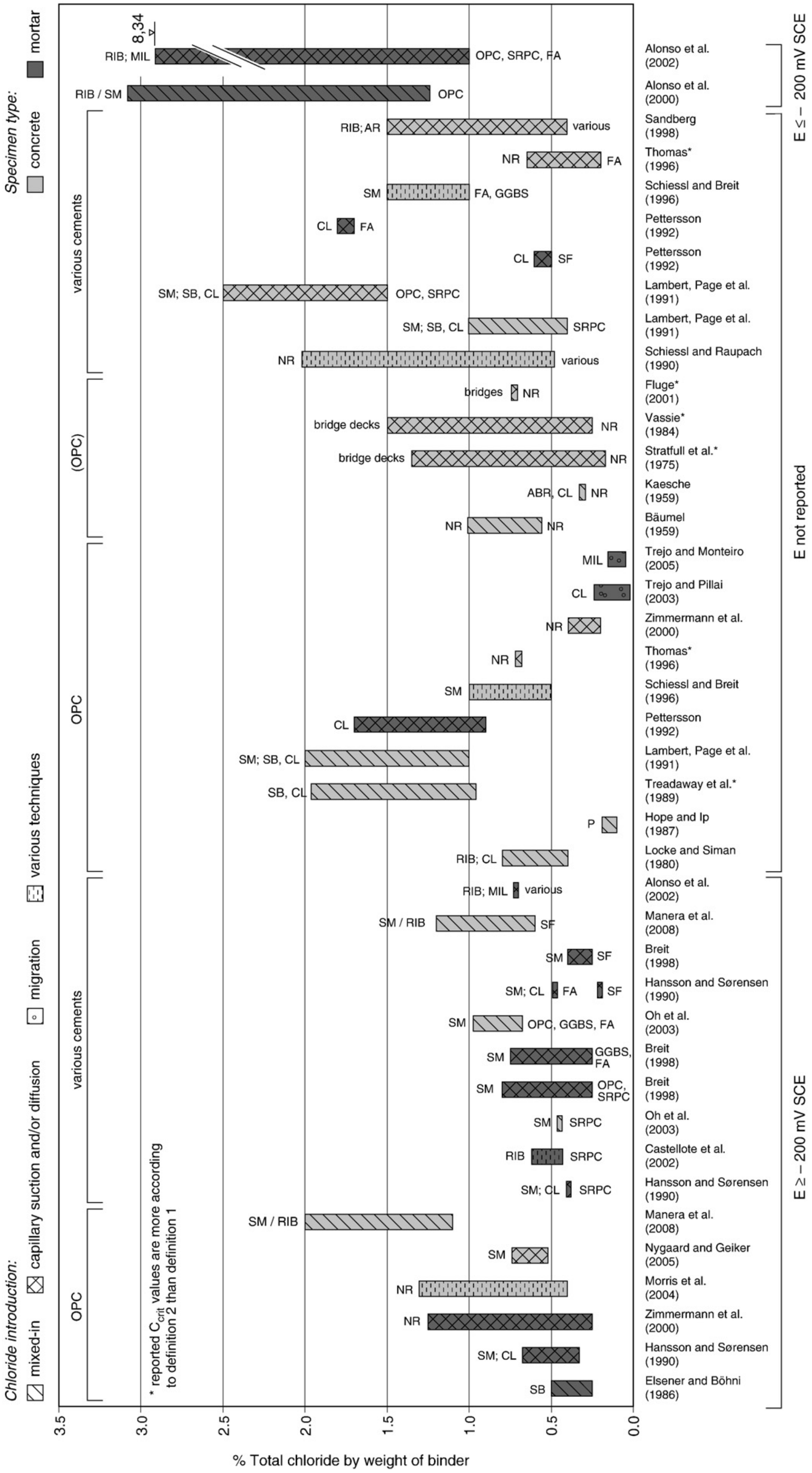

Fig. 2. Reported C_{crit} values presented in terms of total chloride per weight of binder (abbreviations according to Table 5).

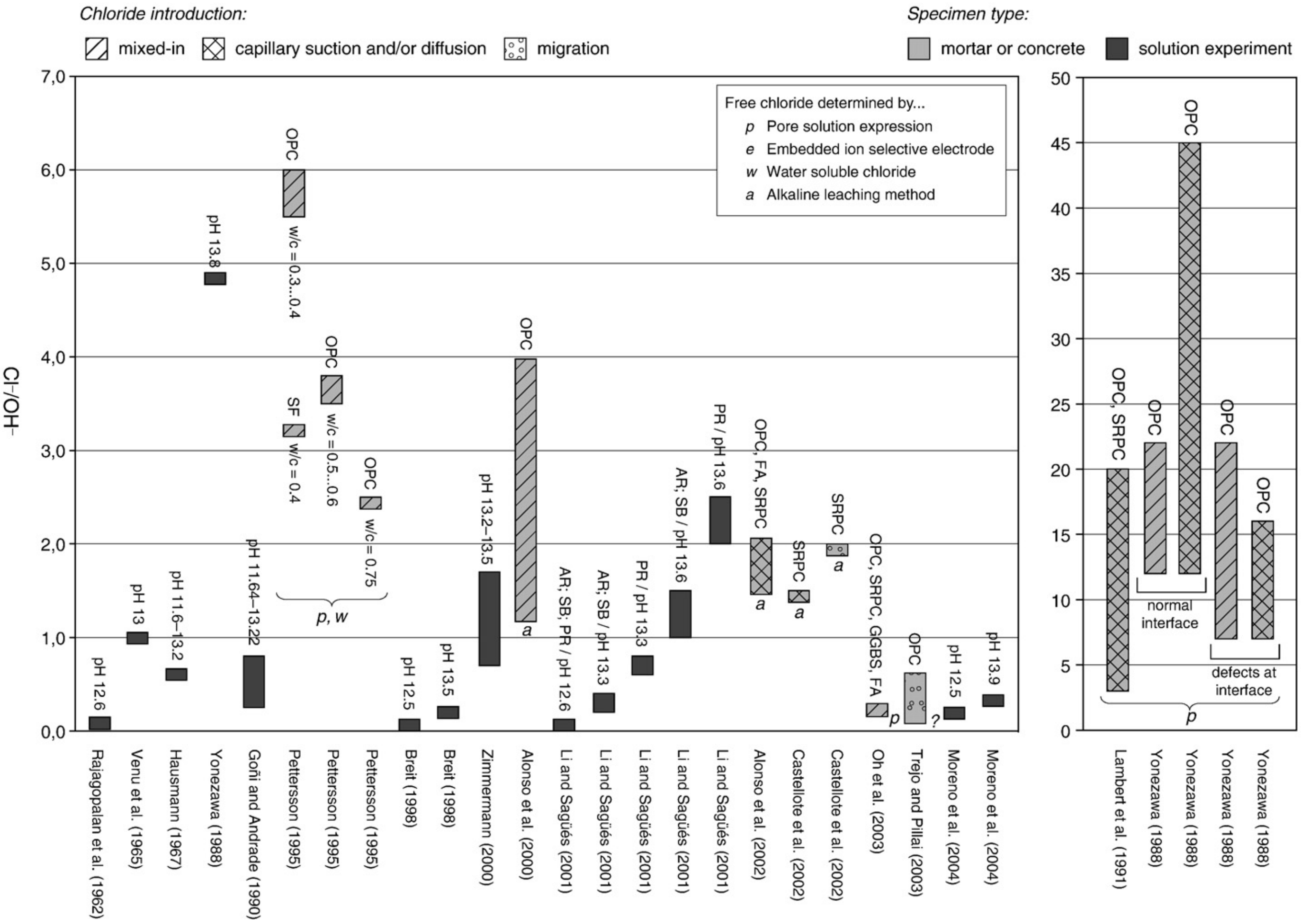

Fig. 3. Reported C_{crit} values presented in terms of Cl^-/OH^- ratio; two separate plots with different ordinates due to large range (abbreviations according to Table 5).

magnitude. In another publication [76], though not directly comparable to the studies reviewed here since it dealt with the corrosion behaviour of steel fibres in concrete, no corrosion was found at Cl^-/OH^- ratios as high as 320. The large scatter in the literature is related to different experimental procedures and the numerous parameters that affect chloride induced corrosion in concrete; this will be discussed in the following sections.

4. Influencing parameters

From an electrochemical point of view, it is the potential of the steel, E_{corr}, relative to the pitting potential, E_{pit}, that determines whether corrosion will start or not. The pitting potential depends on both environmental influences (chloride content) and on properties of the metal such as the degree of alloying (e.g. stainless steel). The open circuit potential of the passive steel, on the other hand, only depends on the environment (pH and oxygen content). Whereas parts of the steel electrode are in contact with the concrete pore liquid, others might be covered with hydration products and thus to a certain extent be shielded from aggressive species in solution. The critical chloride content in concrete is thus not only a matter of pure electrochemistry, but also of physical protection of the steel electrode. Numerous parameters affect the value of C_{crit} and many of them are interrelated [77,78]:

- Steel–concrete interface
- Concentration of hydroxide ions in the pore solution (pH)
- Electrochemical potential of the steel
- Binder type
- Surface condition of the steel
- Moisture content of the concrete
- Oxygen availability at the steel surface
- w/b ratio
- Electrical resistivity of the concrete
- Degree of hydration
- Chemical composition of the steel
- Temperature
- Chloride source (mixed-in initially or penetrated into hardened concrete)
- Type of cation accompanying the chloride ion
- Presence of other species, e.g. inhibiting substances.

It has been suggested to consider the condition of the steel–concrete interface as the most dominating influencing factor [57], together with the pH of the concrete pore solution and the steel potential [78].

The variety of factors involved indicates that the concept of critical chloride content faces some difficulties regarding a unique chloride threshold value applicable to a wide range of structures.

4.1. pH of the pore solution

The presence of Portlandite is the reason for high pH values of ca. 12.5 in the pore solution, whereas NaOH and KOH can increase it to values above 13.5. 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 [79]. The pH of the pore liquid initially mainly depends on the type of binder, but can be affected at later stages as the result of carbonation, leaching, proceeding hydration, etc. The inhibiting effect of hydroxide ions against chloride induced corrosion as a major factor influencing chloride threshold values was early recognised [5,6,8]. The suggestion to present C_{crit} in terms of Cl^-/OH^- ratios reflects this, since in this form the only inhibiting effect is ascribed to the presence of hydroxide ions. It is in this regard often referred to the work by Gouda [8] who experimentally found increasing Cl^-/OH^- ratios with increasing pH, or Hausmann [6] who suggested the famous Cl^-/OH^- ratio of 0.6 based on probability considerations. Fig. 4 illustrates that this value is more a lower boundary than a clear threshold.

4.2. Steel potential

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 (from A to B in Fig. 5). The electrochemical potential of steel at a certain location in a structure is thus of great importance: If the corrosion potential, E_{corr}, is more positive than E_{pit}, pitting corrosion takes place (B), otherwise the influence of chloride is negligible (A). The chloride threshold is thus higher for steel with a more negative potential. This was experimentally confirmed in [43], where 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.

For structures exposed to the atmosphere, the potential of the reinforcement is usually between +100 and −200 mV SCE, whereas for submerged structures it is in the range −400 to −500 mV SCE [78] and consequently higher chloride concentrations can be tolerated. Apart from environmental factors, the steel might be cathodically polarised by an external current, which also alters the critical chloride content (*e.g.* cathodic protection).

4.3. Steel–concrete interface

The importance of the steel–concrete interface for C_{crit} was already mentioned in a publication by Bäumel as early as in 1959 [2]. The author presented a schematic sketch of the interfacial zone and pointed out the protecting character of calcium hydroxide directly surrounding the steel. It was also mentioned that treating the reinforcement with cement slurry prior to embedding can improve the corrosion resistance.

Investigations of the interface between steel and concrete by scanning electron microscopy (SEM) reported by Page have revealed the presence of a dense, lime-rich layer of hydration products on the steel surface [79]. The author postulated that these solid hydration products might buffer the pH in the pore solution, for instance in the case of a local fall in pH in the vicinity of a pit. Furthermore, it was suggested that 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. Experimental work has also shown that the interfacial zone rich in Portlandite limits the diffusion of chloride more effectively than the concrete away from the interface [80]. Several studies confirmed the presence of higher amounts of calcium hydroxide in interfacial zones compared to bulk paste, such as Refs. [81–83]. Contradicting this, no differences between the hydration products in the interfacial zone and those in the bulk cement paste were observed in Ref. [84].

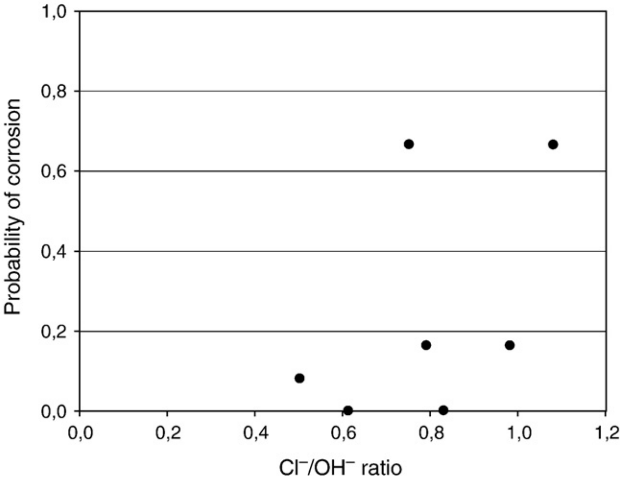

Fig. 4. Results from Hausmann (Table 1 in Ref. [6]) showing the probability of corrosion (number of corroding rods in a set of 12) vs. the Cl^-/OH^- ratio.

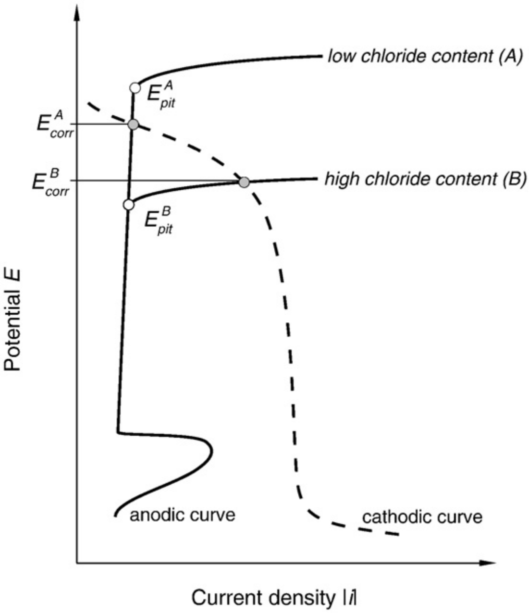

Fig. 5. Influence of chlorides on the anodic polarisation curve, leading to pitting corrosion in situation (B).

It has been reported by Yonezawa et al. [18] that the chloride threshold level was significantly lower when the formation of this lime-rich layer on the steel surface was restricted. Page et al. [24,25] reported Cl^-/OH^- threshold ratios of at least 3 for steel bars embedded in OPC concrete that had been exposed to external chlorides. These C_{crit} values are much higher than those obtained by Hausmann [6] and Gouda [8], a fact that was attributed to the presence of a dense layer of hydration products at the steel–concrete interface in comparison with a steel–solution interface.

In addition to microscopic characteristics, also macroscopic air voids and cracks at the steel–concrete interface affect the onset of corrosion. Macroscopic voids can be the result of incomplete compaction or low workability. Also the orientation of the rebars with respect to the casting direction may lead to gaps between the steel surface and the concrete [83,85] and even the ribs of reinforcement steel may favour the presence of voids. In this context, it was reported that corrosion preferably occurred at the corners or indents of the profiling [21]; Alonso et al. [38] found a higher susceptibility to corrosion for ribbed steel bars in comparison to smooth bars. In a recent study [86] 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) only little corrosion occurred in parts that were subjected to compressive stress, whereas for tensile reinforcement corrosion occurred preferably in the areas most loaded with tension. This observation was explained by mechanical degradation of the steel–concrete interface.

The condition of the interfacial zone appears to have a major influence on the critical chloride content, both on a microscopic and a macroscopic level. However, since it is difficult to measure the amount of entrapped air voids and characterise microscopic defects, the condition of the interface is a property that cannot be quantified.

4.4. Binder type

The type of binder 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. Moreover, certain binders might increase the electrical resistivity of the concrete or improve the characteristics of the steel–concrete interface by forming a denser microstructure.

4.4.1. Chloride binding capacity

The capacity of the hydration products to bind chlorides affects the critical chloride content when expressed in terms of total chlorides. Since bound and free chlorides are suggested to be connected by a chemical equilibrium, also bound chloride presents a corrosion risk by acting as a reservoir of chloride that might dissolve at altered conditions [87–89].

The degree of chloride binding depends on many factors [90] among which some are related to the binder type: The content of C_3A and C_4AF in the cement is a main parameter since the formation of Friedel's salt between chloride and the AFm phases removes considerable amounts of chloride from the pore solution (chemical binding); sulphate resistant Portland cements (SRPC) have thus lower chloride binding capacities [25,47]. Chloride can also be removed from the pore solution due to adsorption to the hydration products (physical binding). Tang and Nilsson [91] reported that the capacity of chloride binding strongly depends on the amount of C–S–H gel in the concrete, regardless of w/c ratio and the amount of aggregates. Binders containing mineral admixtures such as silica fume (SF), pulverized fly ash (FA) or ground granulated blast furnace slag (GGBS) enhance the formation of more gel thereby offering larger surface areas available for adsorption. In addition, fly ash and slag react to calcium aluminate hydrates which also might form Friedel's salt [90]. The mechanism of binding by sorption significantly contributes to chloride binding and might be more important than traditionally assumed [89].

4.4.2. Mineral admixtures

Silica fume. In comparison with ordinary Portland cement (OPC), lower critical chloride contents have been reported for SF containing cement [27,53]; in Ref. [71] slightly higher corrosion rates in SF containing cement were reported. The chloride binding capacity of SF containing cements was reported to be lower compared to OPC [89,92,93]. The partial replacement of OPC with silica fume reduces the amount of aluminate phases and thereby the ability of the cement to bind chloride. But since the addition of SF also leads to a refinement of the pores, the effect of physical adsorption is more pronounced in SF containing binders. However, it was reported that C–S–H produced by the pozzolanic reaction may have lower chloride sorption than C–S–H obtained by hydration of OPC [89]. Owing to the pozzolanic reaction, the alkalinity of the pore solution significantly decreases with increasing addition of silica fume [17]. On the one hand, this affects the chloride binding capacity, since solubility of Friedel's salt increases as the pH of the pore solution decreases [92] (it was observed that the Cl^-/OH^- ratio in the pore solution increased considerably with increasing addition of SF [71,92]), on the other hand, the passive state of the steel will be less stable at a lower pH.

Fly ash. Thomas [31] found lower C_{crit} values for reinforced concrete specimens after exposure to a marine environment for up to four years when they contained FA; the tolerable chloride content decreased with increasing substitution of OPC with FA. Also Oh et al. [47] measured lower chloride thresholds with increasing addition of FA. In contrast, Schiessl and Breit [30] reported higher chloride threshold values for concrete containing FA, and Alonso et al. [43] did not find significant differences in C_{crit} when replacing cement with FA. Fly ash improves the chloride binding capacity of the binder. This can be attributed to both more efficient chemical binding due to higher proportions of active alumina often present in FA [93,94] and better physical adsorption of chloride as the result of more gel produced in the course of hydration [95]. On the other hand, use of FA lowers the pH of the pore liquid [17,96]. In one study, the reduction of pH appeared to be more pronounced than the improved chloride binding capacity and an increased Cl^-/OH^- ratio in the pore solution was found when FA was added to the binder [97].

Blast furnace slag. Gouda and Halaka [9] reported lower chloride threshold values for slag containing concrete specimens in comparison with OPC specimens, whereas Schiessl and Breit [30] found the opposite and Oh et al. [47] did not find a significant effect. The use of GGBS increases the chloride binding capacity due to improved chemical and physical binding [93,98,99]. However, it also 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 (the age of the samples is unfortunately not given in the paper) [100].

4.5. Surface condition of the steel

In many investigations in the laboratory, the reinforcing steel is prepared prior to testing, e.g. by sandblasting or polishing, whereas in practice the reinforcement is used as-received and might be pre-rusted or covered with mill scale. It was shown that the condition of the steel surface has a significant effect on the critical chloride threshold: Mohammed and Hamada [52] 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. The chloride threshold values were sequenced as pre-passivated > black-rusted > polished > brown-rusted > mill-scaled. Also Mammoliti et al. [29] reported higher C_{crit} for polished steel surfaces compared to ground or as-received samples. Li and Sagüés [40] immersed steel bars with different surface conditions in alkaline solutions containing chloride. They investigated steel bars in as-received conditions (mill-scaled), 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. [53] reported a higher critical chloride content for sandblasted steel bars in comparison with steel bars in as-received condition. Mahallati and Saremi [101] found that the presence of mill scale retards the formation and protective characteristics of the passive layer. Gonzales et al. [102] 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 seawater and the rust layer thus contained chloride. Certainly, the presence of chloride affects the process of passivation.

4.6. Influence of other factors

4.6.1. Moisture and oxygen content

Both water and oxygen are required for the corrosion process, thus a lack of one of them is sufficient to inhibit corrosion. Since the moisture content regulates the availability of water and oxygen at the steel surface, it can be regarded as a global, environmental influencing factor for C_{crit}. In the case of water saturated concrete as well as in rather dry concrete, higher chloride concentrations are required to initiate corrosion; the situation most favourable for corrosion initiation is in the range 90–95% RH [66] or concrete exposed to wetting/drying cycles

[103]. The amount of water in the concrete pores also affects the distribution between free and bound chlorides and thus determines the concentration of free chloride in the pore liquid.

4.6.2. Degree of hydration and w/b ratio

The w/b ratio as well as the degree of hydration has an effect on the porosity of the paste and by this the availability of moisture and oxygen at the reinforcement. It was shown that the critical chloride content increases with decreasing w/b ratio [21,27,74] (compare Fig. 3). Both the porosity and the moisture content are reflected by the electrical resistivity, a parameter that has been found to empirically correlate with chloride threshold values in a recent study [48].

4.6.3. Type of chloride salt and chloride source

Several studies have confirmed that calcium chloride leads to more chloride binding than sodium chloride, e.g. [15,93,104]. If C_{crit} is expressed in terms of total chlorides, this theoretically results in higher threshold values. Nevertheless, it was reported that $CaCl_2$ has a much more corrosive effect than NaCl or KCl [15,105]. Care has to be taken, however, when evaluating studies with regard to this: When chloride is added to the mix it acts as an accelerator resulting in a coarser pore structure, which, as was shown earlier, certainly will affect the corrosion behaviour. If the chloride source is seawater, less chloride might be bound due to the inherent sulphates that block some of the adsorption sites [90].

4.7. Overall tendencies in the literature

The values in Fig. 2 were grouped according to the initial free corrosion potential. In many studies, these potentials were higher than −200 mV SCE, where, according to [43], the potential is expected to have little influence on C_{crit}. Unfortunately, the potential was not always reported, but in most of the concerning publications, the exposure conditions indicate that the steel potential was presumably in the same range. In two publications, the steel potential was below −200 mV SCE and significantly higher chloride threshold values were reported.

In Fig. 6, these results were excluded and the scatter of reported C_{crit} values was plotted for some selected parameters. It is apparent that there is no significant difference between mortar and concrete, apart from a somewhat larger range in the case of concrete, but this might simply be owing to more results being available for concrete than for mortar. When analysing different binder types, much more publications reported values for OPC and thus the range is slightly larger compared with SF, FA and GGBS; apart from that, no clear tendencies can be found. In fact, the same is true when examining other characteristics: C_{crit} values scatter over just as large ranges for ribbed and smooth bars, or for conditions such as sandblasted, as-received, polished, etc (Fig. 2). None of these parameters are strong enough to dominate the others.

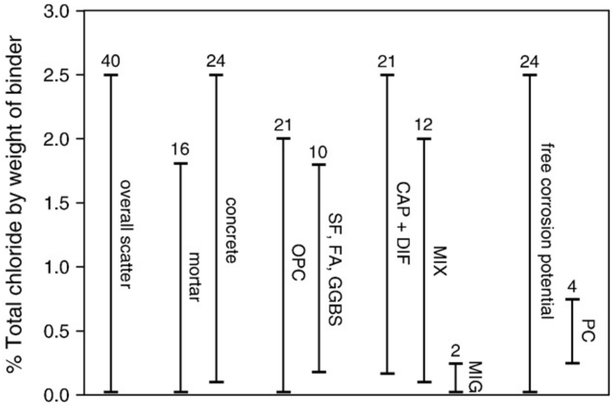

Fig. 6. Scatter of chloride threshold values in the literature sorted by selected parameters and when excluding values obtained at potentials <−200 mV SCE. The numbers above the bars indicate the frequency of occurrence in the literature. Abbreviations according to Table 5.

However, when studying Fig. 3 it is apparent that C_{crit} values obtained from experiments dealing with steel embedded in mortar or concrete exhibit a clear global tendency towards higher C_{crit} values compared with solution experiments. This confirms the importance of the steel–concrete interface as a major influencing parameter. The pH was also mentioned as one of the governing influencing factors and experimental evidence for this is in Fig. 3 apparent from the results by e.g. Li and Sagüés [40] or Moreno et al. [49]. However, the effect is only visible when looking at results derived from a certain experimental setup, i.e. within a certain study, and not when evaluating the results from different authors as a whole. In this case, the effect of the pH is overshadowed by other parameters. As stated above, this is true for most of the influencing factors.

4.8. Summary of influencing parameters

The above discussed interrelations are summarised in Table 6, which is based on a similar compilation in Ref. [57]; in the present article, it was extended to various forms to express C_{crit} and the references were updated. Note that the effect of certain factors is not the same when different forms for expressing the threshold value are chosen.

5. Experimental setups

5.1. General considerations regarding the determination of C_{crit} values

Apart from a suggestion for a method to determine C_{crit} in the field [107], an accepted testing procedure does at present not exist.

Table 6
Effect of influencing factors on the critical chloride content.

Factor	Effect on critical chloride content			References
	Total Cl^- % cem wt	Cl^-/OH^- ratio	Free Cl^-	
Steel condition				
Defects at steel–concrete interface	↓	↓	↓	[18,21,38,86]
Polishing, sandblasting	↑	↑	↑	[29,40,52,53]
Steel potential (>−200 mV SCE)	O	O	O	[43]
Steel potential (<−200 mV SCE)	↓	↓	↓	[43]
Concrete and binder properties				
w/b ratio	↓	↓	↓	[21,27,74]
Chloride binding	↑	O	O	[a]
pH	↑	↑	↑	[5,6,8,40]
Electrical resistivity	↑	↑	↑	[48]
SF	↓	↓	↓	[27,53]
FA	↓↑O[b]	↓O[b]	↓O[b]	[30,31,43,47]
GGBS	↓↑O[b]	O	O	[9,30,47]
SRPC (low C_3A + C_4AF content)	↓	[c]	[c]	[106]
External factors				
Moisture in rather dry concrete	↓	(↓)	(↓)	[66]
Moisture in nearly saturated concrete	↑	↑	↑	[66,79]
Moisture variations	↓	(↓)	(↓)	[103]
Oxygen availability	↓	↓	↓	[6]
Temperature	↓	↓	↓	[28]

↑ (↓) indicates an increase (decrease) in threshold level with an increase of the concerning factor; O means no influence on C_{crit}.

[a] According to theoretical considerations.

[b] Contradictory results reported in the literature.

[c] No results reported.

Experimental setups are thus developed individually. To measure C_{crit} values in the laboratory or on a real structure, such a setup has to include the following [64]:

1. A steel electrode embedded in a cement based material (cement paste, mortar, concrete) or immersed in a solution that simulates the concrete.
2. Chloride ions at the steel surface.
3. A method to detect depassivation of the steel (Definition 1) or for determining if the degree of corrosion has reached the acceptable limit (Definition 2).
4. A method to quantify the chloride content.

Many options exist in order to design an experiment that fulfils these four requirements, as schematically depicted in Fig. 7 [64].

The most convenient setup is a steel electrode immersed in an alkaline solution, where both the chloride concentration and the pH can easily and rapidly be changed and accurately quantified. It is, however, generally agreed that alkaline solutions are not suitable to model real concrete in the laboratory for many reasons. When using cement paste, mortar or concrete, the introduction of chloride into hardened samples becomes more time-consuming; in addition, measuring the concentration actually present at the steel surface is more difficult and laborious. One option is to add chlorides directly to the mix, a common method to simulate the use of chloride bearing aggregates or the addition of $CaCl_2$ as an accelerator as it was done in the past. All these methods normally differ from reality and have thus advantages and disadvantages when modelling the practical situation in the laboratory as summarised in Table 7. For instance, adding chloride to the mix is fast and leads to a homogeneously distributed and thus well-defined total chloride content in the sample; on the other hand, the steel might not passivate if the chloride concentration is too high, more chloride might be bound than in the case of natural chloride penetration into hardened concrete

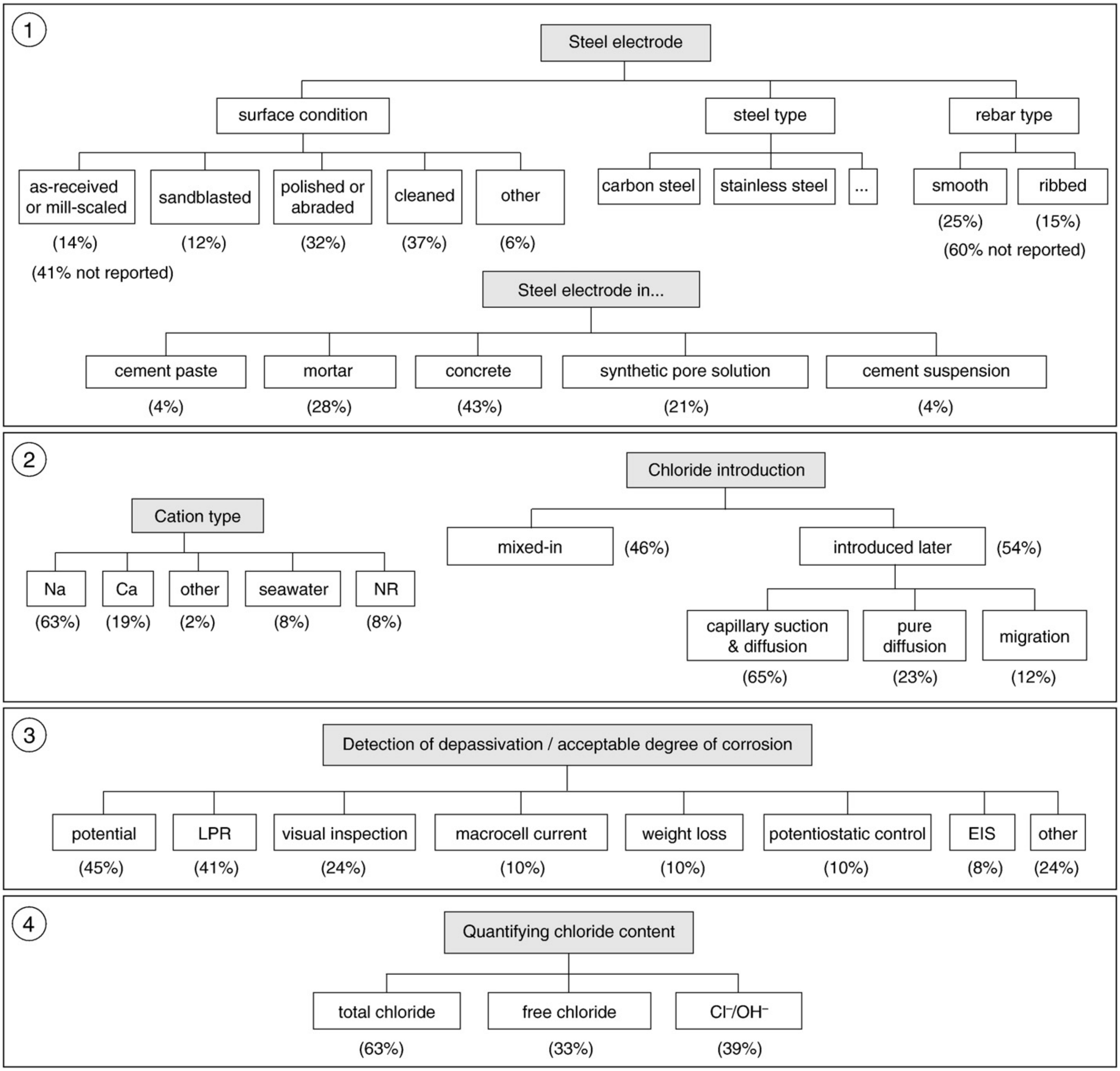

Fig. 7. Experimental possibilities to study critical chloride content (from [64], reprinted with permission).

Table 7
Techniques to introduce chloride into mortar or concrete samples.

Chloride introduction technique	Advantages	Disadvantages
Mixed-in	– Fast	– Initial formation of passive layer questionable
	– Homogeneously distributed	– Homogeneously distributed
	– Total chloride content known	– Different chloride binding
		– Porosity affected
		– Not practice-related (anymore)
Pure diffusion	– Affinity to practice	– Very time-consuming – Sample usually water saturated (limited oxygen availability)
Capillary suction and diffusion	– Affinity to practice	– Time-consuming
	– Faster than pure diffusion	– Drying coarsens the pore structure
Migration	– Fast	– Electrical field – Migration of OH^- ions changes the pH in the sample – Sample water saturated (limited oxygen availability)

and also the porosity of the sample might be affected. While a homogeneous chloride distribution is beneficial for the quantification of the concentration at the steel surface, it is not with regard to modelling a practice-related situation: In contrast to reality, no differential concentration cells are formed along the steel surface, a fact that is certainly important for the onset of pitting corrosion.

Other techniques to introduce chloride are pure diffusion and acceleration by capillary suction (wetting/drying cycles) or an electrical field (migration). Whereas capillary suction and diffusion have a high affinity to practice, migration techniques differ strongly from reality. The most adverse configuration would be to use the rebar of interest directly as anode in order to attract chloride ions, but even if another electrode is applied for this purpose, the presence of the electric field introduces several uncertainties. It is not only chloride ions that migrate, but rather all ions present in the pore solution including those that are generated at anode and cathode. This changes the composition of the pore solution and thus affects critical parameters such as the pH. In fact, Fig. 6 shows that C_{crit} values obtained by the use of migration are significantly lower compared with results from other studies. It should be noted, however, that this observation is only based on two publications [46,51].

Not only the way chloride is introduced, but also the type of salt has an effect on the outcome of experimental work; the same is true for the selection of a certain type of rebar (ribbed or smooth) and its surface condition. These points must be taken into account carefully when designing experiments.

5.2. Methods for detecting active corrosion

5.2.1. Steel potential

Since actively corroding steel has a significantly more negative potential than passive steel in concrete, onset of corrosion can be detected by potential measurements. In this case, a certain shift in potential or an absolute value can be used as criterion for depassivation. Potential measurements are common in field investigations [10,12,36], but are also often used in laboratory research aimed at finding C_{crit} values, as e.g. in Refs. [6,8,9]. It has to be kept in mind that the measured potential is not only dependent on the corrosion state of the steel, but also of other factors such as oxygen availability or iR drops; a low potential value does not necessarily mean significant corrosion. Thus, a clear potential drop (change from passive to active condition) rather than an absolute value should be considered.

5.2.2. Linear polarisation resistance measurements (LPR)

The most accurate technique to detect depassivation of the steel is the measurement of the linear polarisation resistance, which is inversely proportional with the corrosion current as described by the Stern–Geary-equation [108]. The technique is non-destructive and allows the determination of the instantaneous corrosion rate. As criterion for active corrosion, an averaged sustained corrosion rate higher than 0.1… 0.2 $\mu A/cm^2$ has been suggested for concrete containing substantial moisture and oxygen [109]. One of the reasons for this value is the empirical observation that the measured corrosion current in solution and mortar studies was never below 0.1 $\mu A/cm^2$ when rust was observed [110]. One has to be aware, however, that the measured corrosion rate is an average value over the exposed steel area and that the local current density inside a pit is significantly higher. Consequently, the measured value depends strongly on the number and the size of the pits. To avoid such interpretation difficulties, it might be preferred to observe a change in polarisation resistance (or corrosion rate) over time rather than an absolute value.

5.2.3. Electrochemical impedance spectroscopy (EIS)

AC impedance spectroscopy is performed by imposing an external sinusoidal voltage signal of small amplitude over a range of frequencies. The impedance spectra, as derived from the voltage signals and the current responses, are interpreted on the basis of equivalent electrical circuits, which allow determination of e.g. the charge transfer resistance of the process, a parameter that, in many cases, can be equated to the polarisation resistance [111]. By applying the Stern–Geary-equation and assuming Tafel slopes the corrosion rate can then be calculated.

5.2.4. Weight loss

Gravimetric loss of reinforcement can be determined by weighing steel bars prior to embedding and after removing them from concrete. To detect the mass difference, it is required that a significant amount of corrosion has already taken place. This method is thus not suitable to identify the time of depassivation and leads to C_{crit} values according to Definition 2.

Prior to weighing, the bars have to be cleaned to remove any concrete particles. This procedure might result in an additional weight loss. Thomas [31] suggested to apply the cleaning procedure also to control rebars to find this “processing weight loss”.

5.2.5. Other methods

The corrosion rate can be determined by measuring the *macro-cell current* between the electrode of interest and an auxiliary electrode acting as cathode as e.g. in Refs. [22,30,37,39].

In some cases the working electrode is polarised and held constant at a certain potential during the experiments (*potentiostatic control*) [21,34,43,50]; the current required for this polarisation is monitored until an increase indicates active corrosion. Depassivation can also be detected by means of *galvanostatic polarisation*: A fixed anodic current is applied and the potential response is monitored vs. time. The measured curve gives information on the corrosive or inhibitive character of a certain environment. Though rarely, this method has been used to determine C_{crit} values [4,5,8,9].

It has to be noted that controlling the steel potentiostatically (or galvanostatically) does not provide realistic conditions. Under the externally applied current, the entire steel surface exhibits the same potential, which is — in the case of potentiostatic control — determined by an infinitely strong cathode. No differential aeration cells are formed, although in reality, these have to provide a current strong enough for pitting corrosion initiation [112]. In addition, a critical parameter with this method is the selection of the potential to which the working electrode is polarised (or in the case of galvanostatic polarisation the current density). It might be interesting to note in this context that C_{crit} values obtained from test setups using potentiostatic control are generally lower compared with those obtained on rebars without external polarisation (Fig. 6).

It is of course also possible to measure complete polarisation curves, or only the anodic part, in order to determine pitting potentials. Such E–i–curves can be measured by either stepwise impressing a fixed current until a certain potential is reached (*galvanodynamic polarisation*), or by controlling the potential and measuring the corresponding current (*potentiodynamic polarisation*).

Finally, if the concrete is split and the steel exposed, *visual inspection* of the steel surface can help to identify depassivation with the appearance of rust on the steel surface. The accuracy of the method is 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 was mostly used in early work on corrosion initiation [7] and in field studies [41]; sometimes it was applied in combination with other techniques, e.g. in [6,13,16].

All of the techniques mentioned have in common that a certain amount of corrosion is necessary to detect depassivation. Depassivation is not considered as an instant event, but rather as a period of time during which the depassivation process takes place from the first defect until active corrosion is established [77]. It is impossible to identify the very start, e.g. the first local defect in the passive film. Electrochemical techniques come much closer to this moment than visual inspection and weight loss measurements. This should be kept in mind when considering the definitions of C_{crit} as described in Section 2.1.

5.3. Methods for determining the total chloride content

The analysis of total chloride is frequently applied in practice and well documented in standards, such as [68,69]. The total chloride content in concrete is usually determined by analysing cores drilled from hardened concrete, which are cut into slices of a certain thickness to obtain a chloride profile. The sample is then crushed, powdered and homogenised and subsequently dissolved in dilute nitric acid. The chloride concentration in the extraction solution can be determined by several techniques such as titration, use of ion selective electrodes or spectrophotometric methods. Dhir et al. [113] compared various methods to determine the total chloride content in concrete on OPC concrete specimens with mixed-in chloride. They found that the quantity of chloride extracted depends on the strength of the nitric acid and dissolution time. The results also suggested that the acid extraction technique cannot completely dissolve all the chlorides from the powder samples; values in the range 70… 90% of the true content were reported. A more expensive but very accurate way is to determine the total chloride content in concrete powder samples by X-ray fluorescence spectrometry (XRF) [113]. In a recent round robin test [114] involving 30 laboratories methods for the analysis of total chloride were compared and a good reproducibility was found for all of the methods.

5.4. Methods for determining the free chloride content

5.4.1. Pore solution expression

The technique of expressing pore water from cement paste or mortar is well established and has been used by many researchers, e.g. [115,116]. It is probably the most accepted method to determine the free chloride content in the pore solution. However, the application is limited when mortar with lower w/c ratios, coarse aggregate particles or rather dry specimens are investigated [117]. It has been noted that under the pressure “loosely bound chloride” might be released and thus result in an overestimation of the free chloride content [118]. Also other studies reported that the chloride concentration in the liquid expressed from samples that had been immersed in solutions was higher than the concentration in the exposure solution [89,116]. It has also 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 leads to inaccurate results.

5.4.2. Leaching techniques

Leaching techniques are based on mixing crushed or ground samples with a solvent and measuring the amount of chloride passing into solution. Distilled water is usually used as solvent. Alternatives such as methanol or ethyl alcohol have been investigated but both proved to be extremely ineffective at leaching out the free chlorides; measured concentrations were in the range of 5… 10% of the free chloride concentration obtained from pore solution expression [116,119]. The amount of leached chloride appears to depend on the time during which the sample is in contact with the leaching media and on temperature. Arya et al. [119] investigated different extraction procedures in this regard and compared the results 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 [117] 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 to select an accurate leaching procedure and that thus the leaching technique is not practical for determining the free chloride content. Castellote et al. [120] presented a method based on an alkaline solvent to extract the free chloride. Good agreement with pore water expression was found. However, rather high chloride contents have been investigated (up to 6% by weight of sample) and it might be questionable if the technique is also accurate at lower and more practical concentrations.

The chloride concentrations obtained from leaching methods are sometimes referred to as *water soluble chloride* (if water is the solvent) and often considered to be equal to *free chloride*. Contrary to Europe, water soluble chloride analysis is a standard method used in North America [121]: In the “Soxhlet extraction technique” boiling water is used to extract chloride from concrete chips.

5.4.3. Ion selective electrodes

The free chloride content in the pore solution can also be measured by the use of ion selective electrodes embedded in the concrete [32,122,123]. A major advantage of this technique is that it measures non-destructively and thus allows continuous monitoring of the chloride concentration in the concrete pore solution. Moreover, results are obtained highly localised, whereas the above mentioned techniques require comparatively large samples volumes for the analysis and thus result in average values.

5.5. Experimental setups in the literature

The percentages given in Fig. 7 represent the proportion of experiments, in which the corresponding configuration was chosen. For example, in 25% of the experiments evaluated in the present literature review, smooth steel was used, while in 15% the bars were ribbed; in 60% no details with regard to this were given in the publication. Note that “experiments” rather than publications have been counted (meaning that one publication might contain several different experiments) and that the sum of the percentages can be higher than 100%, as e.g. in the case of corrosion detection techniques, since in some experiments more than only one technique was applied.

In addition, one has to be aware that an evaluation of this kind cannot be accurate as in some studies hundreds of samples have been tested, while other reported results from very limited amounts of samples. Nevertheless, it gives an impression of preferably used setups.

Concerning the steel electrode, often smooth steel with a prepared surface was investigated: in nearly 40% of the experiments the steel was cleaned and degreased and in ca. 30% polishing or abrading was used to prepare the steel surface; in only 14% the steel was reported to have been investigated in as-received or mill-scaled condition. Without doubt this affects the characteristics of the steel–concrete interface, one of the major influencing factors for C_{crit} as was shown earlier. In ca. 20% the steel was investigated directly immersed in synthetic pore solution; also this does not give a realistic interface, but it allows comparatively simple measurements of hydroxide and free chloride ion concentrations and fast experimental programmes. As in the case of steel embedded in mortar or concrete, chloride introduction can be time-consuming, in nearly 50% of the evaluated experiments chloride has been added directly to the fresh mix; in the case of hardened samples, a combination of capillary suction and diffusion appears to be the most often used technique to introduce chloride. In more than 60% of the experiments C_{crit} was reported in terms of total chloride relative to the binder weight, but when excluding the experiments with the steel electrode directly immersed in solution, this figure is as high as 84%. Free chloride concentrations or $\mathrm{Cl}^-/\mathrm{OH}^-$ ratios have only been determined in a minority of experiments involving hardened samples, and, in addition, these were often porous mortar rather than concrete samples. Reliable C_{crit} values in terms of both total and free chloride contents for dense concrete are lacking.

A wide variety of testing setups is beneficial when exploring the issue of C_{crit} from different perspectives; in fact, varying parameters is even required when specifically investigating certain influences as e.g. the surface condition of the steel. On the other hand, different test setups make comparison of the results difficult. With regard to a practical and relatively fast test it is also favoured to simplify reality and e.g. use mixed-in chloride; in order to obtain reproducible results the surface might be polished or sandblasted. However, the results of such studies cannot be carried over into practice.

6. Evaluation with regard to chloride binding

In the literature review in Ref. [70] Glass and Buenfeld evaluated data by Lambert et al. [25] and pointed out that $\mathrm{Cl}^-/\mathrm{OH}^-$ threshold ratios span a larger range (from 3 to 20) in comparison with corresponding total chloride contents (from 1.5 to 2.5%). More publications are now available reporting C_{crit} values in terms of total and free chloride or $\mathrm{Cl}^-/\mathrm{OH}^-$ ratios and they confirm this finding without exception as illustrated in Fig. 8. For example, Pettersson [26] reported total chloride threshold values from 0.9 to 1.4% by weight of binder (for OPC) and corresponding free chloride threshold concentrations from 36 to 73.9 g/l. The lowest total chloride content (0.9%) is 64% of the highest value (1.4%), whereas the lowest free chloride content (36 g/l) is 49% of the highest value (73.9 g/l). In Fig. 8 these percentages are plotted on a reverse y-axis where the height of the bars indicates the range of reported values, i.e. the higher the bar the larger the span. Also when looking at C_{crit} values reported in the literature as a whole (Tables 2–4), values in terms of total chloride per binder weight span a smaller range than free chloride concentrations or $\mathrm{Cl}^-/\mathrm{OH}^-$ threshold ratios. It was suggested in Ref. [70] 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. In addition, when assuming that only the free chloride is relevant for corrosion initiation, the following is expected: forms to express C_{crit} that ignore bound chloride, such as $\mathrm{Cl}^-/\mathrm{OH}^-$ ratios or free chloride by mass of cement, should theoretically result in a smaller range of values. In the available data, however, the opposite was found. Based on this observation, Glass and Buenfeld [70] questioned the importance of chloride binding and postulated that bound chloride plays a more important role in corrosion initiation than generally assumed. The additional data evaluated in the present review appears to support this observation: the same was found even when different techniques to measure the free chloride content were applied (as indicated above the bars in Fig. 8).

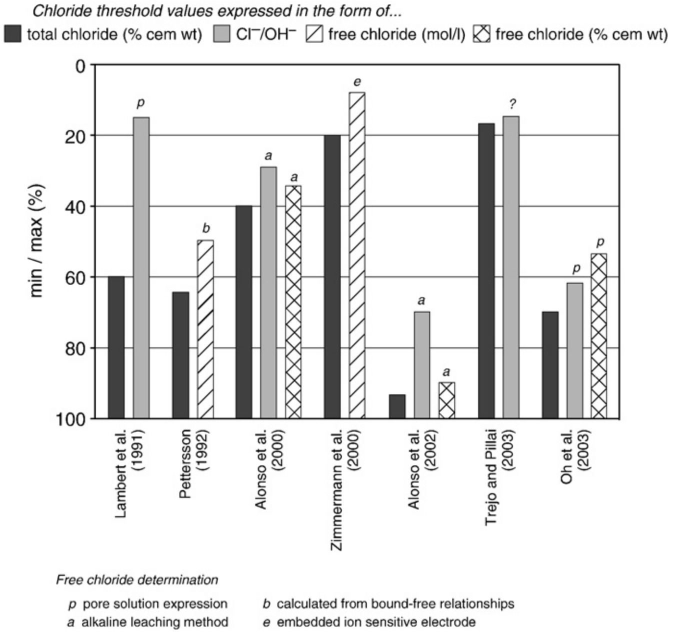

Fig. 8. Range of reported C_{crit} values for both mortar and concrete expressed in different forms.

In the light of the uncertainties associated with measurement techniques for the free chloride concentration as discussed in Section 5.4, one should, however, also consider the reliability and accuracy of the reported free chloride concentrations. All of the procedures used to quantify free chloride contents are likely to lead to a scatter in the results, which could at least partly explain the larger range of reported free chloride concentrations compared with total chloride contents.

7. Conclusions

From the present literature review, the following major conclusions are drawn:

1. The critical chloride content in reinforced concrete can and has been studied by many different experimental setups. When evaluating the entirety of reported results in the literature, it appears that certain parameters inherent to the test procedure (such as the application of an electric field to accelerate chloride ingress or potentiostatic control of the rebar) can have a more dominant influence on the result than the parameters under investigation (e.g. binder type). Many of the used experimental setups are not suited to give realistic results. In addition, comparison of the reported values is difficult owing to differences in procedures. On this basis, it is not possible to select a reliable range of chloride threshold values and thus the current practice of condition assessment as well as service life design cannot be improved.
2. Consultant engineers thus still base their decisions on long-term experience from existing structures, of which most were built with ordinary Portland cement. However, more and more non-traditional cements containing pozzolanic materials or other additions are used. The effect of some of these materials — namely SF, FA, and GGBS — has been studied several times, but the results were often

contradictory and/or cannot be transferred to real structures due to unrealistic testing conditions. Regarding reinforcement corrosion, the behaviour of the mentioned pozzolanas, but also many other upcoming cementing materials, is completely unknown.

3. In the light of Conclusions 1 and 2, there is a strong need for a practice-related test method. For a procedure that realistically models corrosion of reinforced concrete structures exposed to seawater or deicing salt spray, the authors suggest the following experimental parameters: The rebar has to be *ribbed* and in *as-received* condition, and must be *embedded in concrete* (or at least mortar). Chloride has to be introduced by a combination of *capillary suction and diffusion* and must not be added to the fresh mix. Depassivation is best detected by electrochemical measurements in order to stick to a precise definition of C_{crit} (Definition 1). In this regard measurement of *steel potential*, *linear polarisation resistance*, or *electrochemical impedance spectroscopy* are appropriate methods; potentio- or galvanostatic (or -dynamic) polarisation is not suitable.
4. The most important influencing factors on C_{crit} are the steel–concrete interface and the steel potential, since these are the only parameters standing out when comparing the reported results as a whole. All the other parameters are interrelated and overlap each other in such a way that no overall trends are visible.
5. More research is needed regarding the importance of chloride binding. For this purpose, however, reliable methods to measure the free chlorides are required. At present, these techniques are associated with uncertainties and might at least partly be responsible for the inconsistency between the general assumption that bound chlorides are rendered harmless and experimental results in the literature.

Acknowledgements

The authors acknowledge the support of COIN (www.sintef.no/coin).

References

[1] H. Kaesche, Die Prüfung der Korrosionsgefährdung von Stahlarmierungen durch Betonzusatzmittel, Zement-Kalk-Gips 7 (1959) 289–294.
[2] A. Bäumel, Die Auswirkung von Betonzusatzmitteln auf das Korrosionsverhalten von Stahl in Beton, Zement-Kalk-Gips 7 (1959) 294–305.
[3] D.A. Lewis, W.J. Copenhagen, Corrosion of reinforcing steel in concrete in marine atmospheres, Corrosion 15 (1959) 382–388.
[4] K.S. Rajagopalan, K. Venu, K. Balakrishnan, Anodic polarization studies in neutral and alkaline solutions containing corrosion inhibitors. I. NaOH–NaCl system, Journal of the Electrochemical Society 109 (1962) 81–87.
[5] K. Venu, K. Balakrishnan, K.S. Rajagopalan, A potentiokinetic polarization study of the behaviour of steel in NaOH–NaCl system, Corrosion Science 5 (1965) 59–69.
[6] D.A. Hausmann, Steel corrosion in concrete. How does it occur? Materials Protection 6 (1967) 19–23.
[7] W. Richartz, Die Bindung von Chlorid bei der Zementerhärtung, Zement-Kalk-Gips 10 (1969) 447–456.
[8] V.K. Gouda, Corrosion and corrosion inhibition of reinforcing steel. I. Immersed in alkaline solutions, British Corrosion Journal 5 (1970) 198–203.
[9] V.K. Gouda, W.Y. Halaka, Corrosion and corrosion inhibition of reinforcing steel, II. Embedded in concrete, British Corrosion Journal 5 (1970) 204–208.
[10] R.F. Stratfull, W.J. Jurkovich, D.L. Spellman, Corrosion testing of bridge decks, Transportation Research Record 539 (1975) 50–59.
[11] C.E. Locke, A. Siman, Electrochemistry of reinforcing steel in salt-contaminated concrete, in: D.E. Tonini, J.M. Gaidis (Eds.), Corrosion of Reinforcing Steel in Concrete, ASTM STP 713, American Society for Testing and Materials, 1980, pp. 3–16.
[12] P. Vassie, Reinforcement corrosion and the durability of concrete bridges, Proceedings of the Institution of Civil Engineers Part 1 (76) (1984) 713–723.
[13] B. Elsener, H. Böhni, Corrosion of steel in mortar studied by impedance measurements, Electrochemical Methods in Corrosion Research, in: M. Duprat (Ed.), Materials Science Forum 8, 1986, pp. 363–372.
[14] S. Diamond, Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures, Cement, Concrete, and Aggregates 8 (1986) 97–102.
[15] C. Andrade, C.L. Page, Pore solution chemistry and corrosion in hydrated cement systems containing chloride salts: a study of cation specific effects, British Corrosion Journal 21 (1986) 49–53.
[16] B.B. Hope, A.K.C. Ip, Chloride corrosion threshold in concrete, ACI Materials Journal (July–August 1987) 306–314.
[17] K. Byfors, Influence of silica fume and flyash on chloride diffusion and pH values in cement paste, Cement and Concrete Research 17 (1987) 115–130.
[18] T. Yonezawa, V. Ashworth, R.P.M. Procter, Pore solution composition and chloride effects on the corrosion of steel in concrete, Corrosion 44 (1988) 489–499.
[19] K.W.J. Treadaway, R.N. Cox, B.L. Brown, Durability of corrosion resisting steels in concrete, Proceedings of the Institution of Civil Engineers Part 1 (86) (1989) 305–331.
[20] S. Goñi, C. Andrade, Synthetic concrete pore solution chemistry and rebar corrosion rate in the presence of chlorides, Cement and Concrete Research 20 (1990) 525–539.
[21] C.M. Hansson, B. Sørensen, The threshold concentration of chloride in concrete for the initiation of reinforcement corrosion, in: N.S. Berke, V. Chaker, D. Whiting (Eds.), Corrosion rates of steel in concrete, ASTM STP 1065, 1990, pp. 3–16.
[22] P. Schiessl, M. Raupach, Influence of concrete composition and microclimate on the critical chloride content in concrete, Proc. 3rd Int. Symp. "Corrosion of Reinforcement in Concrete", Elsevier Applied Science, Wishaw, UK, 1990, pp. 49–58.
[23] M.D.A. Thomas, J.D. Matthews, C.A. Haynes, Chloride diffusion and reinforcement corrosion in marine exposed concrete containing pulverized-fuel ash, Proc. 3rd Int. Symp. "Corrosion of Reinforcement in Concrete", Elsevier Applied Science, Wishaw, UK, 1990, pp. 198–212.
[24] C.L. Page, P. Lambert, P.R.W. Vassie, Investigations of reinforcement corrosion. 1. The pore electrolyte phase in chloride-contaminated concrete, Materials and Structures 24 (1991) 243–252.
[25] P. Lambert, C.L. Page, P.R.W. Vassie, Investigations of reinforcement corrosion. 2. Electrochemical monitoring of steel in chloride-contaminated concrete, Materials and Structures 24 (1991) 351–358.
[26] K. Pettersson, Corrosion threshold value and corrosion rate in reinforced concrete, CBI report 2:92, Swedish Cement and Concrete Research Institute, 1992.
[27] K. Pettersson, Chloride threshold value and the corrosion rate in reinforced concrete, Proc. of the Nordic Seminar, Lund, 1995, pp. 257–266.
[28] S.E. Hussain, A. Rasheeduzzafar, A. Al-Musallam, A.S. Al-Gahtani, Factors affecting threshold chloride for reinforcement corrosion in concrete, Cement and Concrete Research 25 (1995) 1543–1555.
[29] L.T. Mammoliti, L.C. Brown, C.M. Hansson, B.B. Hope, The influence of surface finish of reinforcing steel and pH of the test solution on the chloride threshold concentration for corrosion initiation in synthetic pore solutions, Cement and Concrete Research 26 (1996) 545–550.
[30] P. Schiessl, W. Breit, Local repair measures at concrete structures damaged by reinforcement corrosion — aspects of durability, Proc. 4th Int. Symp. "Corrosion of Reinforcement in Concrete Construction", The Royal Society of Chemistry, Cambridge, 1996, pp. 525–534.
[31] M. Thomas, Chloride threshold in marine concrete, Cement and Concrete Research 26 (1996) 513–519.
[32] B. Elsener, L. Zimmermann, D. Flückiger, D. Bürchler, H. Böhni, Chloride penetration — non destructive determination of the free chloride content in mortar and concrete, Proc. RILEM Int. Workshop "Chloride penetration into concrete", Paris, 1997.
[33] P. Sandberg, K. Pettersson, H.E. Sørensen, H. Arup, Critical chloride concentrations for the onset of active reinforcement corrosion, Proc. RILEM Int. Workshop "Chloride penetration into concrete" Paris, 1997.
[34] W. Breit, Critical chloride content — investigations of steel in alkaline chloride solutions, Materials and Corrosion 49 (1998) 539–550.
[35] W. Breit, Kritischer korrosionsauslösender Chloridgehalt — Neuere Untersuchungsergebnisse (Teil 2), Beton 8 (1998) 511.
[36] P. Sandberg, Chloride initiated reinforcement corrosion in marine concrete, Dissertation (Report TVBM-1015), Lund Institute of Technology, Division of Building Materials, Lund University, 1998.
[37] L. Zimmermann, B. Elsener, H. Böhni, Critical factors for the initiation of rebar corrosion, Proc. EUROCORR '99, European Federation of Corrosion, Aachen, Germany, 1999.
[38] C. Alonso, C. Andrade, M. Castellote, P. Castro, Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar, Cement and Concrete Research 30 (2000) 1047–1055.
[39] L. Zimmermann, Korrosionsinitiierender Chloridgehalt von Stahl in Beton, Dissertation, ETH Nr. 13870, ETH Zürich, 2000.
[40] L. Li, A.A. Sagüés, Chloride corrosion threshold of reinforcing steel in alkaline solutions — open-circuit immersion tests, Corrosion 57 (2001) 19–28.
[41] F. Fluge, Marine chlorides — a probabilistic approach to derive provisions for EN 206-1, Third Workshop on "Service Life Design of Concrete Structures — From Theory to Standardisation", DuraNet, Tromsø, 2001, pp. 63–83.
[42] M. Castellote, C. Andrade, C. Alonso, Accelerated simultaneous determination of the chloride depassivation threshold and of the non-stationary diffusion coefficient values, Corrosion Science 44 (2002) 2409–2424.
[43] C. Alonso, M. Castellote, C. Andrade, Chloride threshold dependence of pitting potential of reinforcements, Electrochimica Acta 47 (2002) 3469–3481.
[44] O. de Rincón, Y. Hernández, R. Fernández, M. Morales, K. Inciarte, Comparison between chloride ion threshold and electrochemical measurements for reinforcement corrosion, Proc. 3rd RILEM Int. Workshop "Testing and Modelling the Chloride Ingress into Concrete", Madrid, 2002.
[45] W. Morris, A. Vico, M. Vazquez, S.R. de Sanchez, Corrosion of reinforcing steel evaluated by means of concrete resistivity measurements, Corrosion Science 44 (2002) 81–99.
[46] D. Trejo, R.G. Pillai, Accelerated chloride threshold testing: Part I — ASTM A 615 and A 706 reinforcement, ACI Materials Journal 100 (2003) 519–527.

[47] B.H. Oh, S.Y. Jang, Y.S. Shin, Experimental investigation of the threshold chloride concentration for corrosion initiation in reinforced concrete structures, Magazine of Concrete Research 55 (2003) 117–124.

[48] W. Morris, A. Vico, M. Vázquez, Chloride induced corrosion of reinforcing steel evaluated by concrete resistivity measurements, Electrochimica Acta 49 (2004) 4447–4453.

[49] M. Moreno, W. Morris, M.G. Alvarez, G.S. Duffó, Corrosion of reinforcing steel in simulated concrete pore solutions: effect of carbonation and chloride content, Corrosion Science 46 (2004) 2681–2699.

[50] P.V. Nygaard, M.R. Geiker, A method for measuring the chloride threshold level required to initiate reinforcement corrosion in concrete, Materials and Structures 38 (2005) 489–494.

[51] D. Trejo, P.J. Monteiro, Corrosion performance of conventional (ASTM A615) and low-alloy (ASTM A706) reinforcing bars embedded in concrete and exposed to chloride environments, Cement and Concrete Research 35 (2005) 562–571.

[52] T.U. Mohammed, H. Hamada, Corrosion of steel bars in concrete with various steel surface conditions, ACI Materials Journal 103 (2006) 233–242.

[53] M. Manera, Ø. Vennesland, L. Bertolini, Chloride threshold for rebar corrosion in concrete with addition of silica fume, Corrosion Science 50 (2008) 554–560.

[54] J. Gulikers, Considerations on the reliability of service life predictions using a probabilistic approach, Journal de Physique IV (136) (2006) 233–241.

[55] J. Gulikers, Probabilistic service life modelling of concrete structures: improvement or unrealistic? CONSEC'07, Proceedings of the 5th International Conference on Concrete Under Severe Conditions, Environment and Loading, Tours, France, 2007, pp. 891–902.

[56] K.Y. Ann, H.-W. Song, Chloride threshold level for corrosion of steel in concrete, Corrosion Science 49 (2007) 4113–4133.

[57] G.K. Glass, N.R. Buenfeld, Chloride threshold levels for corrosion induced deterioration of steel in concrete, Proc. RILEM Int. Workshop "Chloride Penetration into Concrete", Paris, 1997, p. 429.

[58] W. Breit, Kritischer korrosionsauslösender Chloridgehalt – Sachstand (Teil 1), Beton 7 (1998) 442.

[59] RILEM, Draft recommendation for repair strategies for concrete structures damaged by reinforcement corrosion, Materials and Structures 27 (1994) 415–436.

[60] Model code for service life design, fib Bulletin No. 34, 2006.

[61] L. Bertolini, F. Bolzoni, T. Pastore, P. Pedeferri, Behaviour of stainless steel in simulated concrete pore solution, British Corrosion Journal 31 (1996) 218–222.

[62] D. Trejo, R.G. Pillai, Accelerated chloride threshold testing — Part II: corrosion-resistant reinforcement, ACI Materials Journal 101 (2004) 57–64.

[63] H. Yu, W.H. Hartt, Effects of reinforcement and coarse aggregates on chloride ingress into concrete and time-to-corrosion: Part 1 — spatial chloride distribution and implications, Corrosion 63 (2007) 843–849.

[64] U. Angst, Ø. Vennesland, Critical chloride content in concrete — state of the art, in: Concrete Repair, Rehabilitation and Retrofitting II. Proceedings of the 2nd Int. Conf. on Concrete Repair, Rehabilitation and Retrofitting, Cape Town, South Africa, CRC Press/Balkema, The Netherlands, 2008, p. 149.

[65] C.L. Page, K.W.J. Treadaway, Aspects of the electrochemistry of steel in concrete, Nature 297 (1982) 109–114.

[66] P. Schiessl, S. Lay, Influence of concrete composition, in: H. Böhni (Ed.), Corrosion in Reinforced Concrete Structures, Woodhead Publishing Limited, Cambridge, 2005, pp. 91–134.

[67] K. Tuutti, Corrosion of Steel in Concrete, Swedish Cement and Concrete Research Institute, 1982.

[68] ASTM C-1152. Standard test method for acid-soluble chloride in mortar and concrete, American Society for Testing and Materials.

[69] C. Andrade, M. Castellote, Recommendation of RILEM TC 178-TMC: "Testing and modelling chloride penetration in concrete": analysis of total chloride content in concrete, Materials and Structures 35 (2002) 583–585.

[70] G.K. Glass, N.R. Buenfeld, The presentation of the chloride threshold level for corrosion of steel in concrete, Corrosion Science 39 (1997) 1001–1013.

[71] C.L. Page, J. Havdahl, Electrochemical monitoring of corrosion of steel in microsilica cement pastes, Materials and Structures 18 (1985) 41–47.

[72] G. Sergi, G.K. Glass, A method of ranking the aggressive nature of chloride contaminated concrete, Corrosion Science 42 (2000) 2043–2049.

[73] G.K. Glass, B. Reddy, N.R. Buenfeld, Corrosion inhibition in concrete arising from its acid neutralisation capacity, Corrosion Science 42 (2000) 1587–1598.

[74] O. Poupard, A. Aït-Mokhtar, P. Dumargue, Corrosion by chlorides in reinforced concrete: determination of chloride concentration threshold by impedance spectroscopy, Cement and Concrete Research 34 (2004) 991–1000.

[75] European Standard EN 206-1, Concrete — Part 1: Specification, Performance, Production and Conformity, European Committee for Standardisation, 2000.

[76] P.S. Mangat, K. Gurusamy, Corrosion resistance of steel fibres in concrete under marine exposure, Cement and Concrete Research 18 (1988) 44–54.

[77] R. Cigna, C. Andrade, U. Nürnberger, R. Polder, R. Weydert, E. Seitz (Eds.), COST 521: Final Report "Corrosion of Steel in Reinforced Concrete Structures", Luxembourg, 2002.

[78] L. Bertolini, B. Elsener, P. Pedeferri, R. Polder, Corrosion of Steel in Concrete, WILEY VCH, 2004.

[79] C.L. Page, Mechanism of corrosion protection in reinforced concrete marine structures, Nature 258 (1975) 514–515.

[80] C.L. Page, N.R. Short, A. El Tarras, Diffusion of chloride ions in hardened cement pastes, Cement and Concrete Research 11 (1981) 395–406.

[81] M.N. Al Khalaf, C.L. Page, Steel/mortar interfaces: microstructural features and mode of failure, Cement and Concrete Research 9 (1979) 197–207.

[82] L. Yue, H. Shuguang, The microstructure of the interfacial transition zone between steel and cement paste, Cement and Concrete Research 31 (2001) 385–388.

[83] A.T. Horne, I.G. Richardson, R.M.D. Brydson, Quantitative analysis of the microstructure of interfaces in steel reinforced concrete, Cement and Concrete Research 37 (2007) 1613–1623.

[84] G.K. Glass, R. Yang, T. Dickhaus, N.R. Buenfeld, Backscattered electron imaging of the steel–concrete interface, Corrosion Science 43 (2001) 605–610.

[85] T.U. Mohammed, H. Hamada, A discussion of the paper "Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar" by C. Alonso, C. Andrade, M. Castellote and P. Castro, Cement and Concrete Research 31 (2001) 835–838.

[86] A. Castel, T. Vidal, R. François, G. Arliguie, Influence of steel–concrete interface quality on reinforcement corrosion induced by chlorides, Magazine of Concrete Research 55 (2003) 151–159.

[87] G.K. Glass, B. Reddy, N.R. Buenfeld, The participation of bound chloride in passive film breakdown on steel in concrete, Corrosion Science 42 (2000) 2013–2021.

[88] B. Reddy, G.K. Glass, P.J. Lim, N.R. Buenfeld, On the corrosion risk presented by chloride bound in concrete, Cement & Concrete Composites 24 (2002) 1–5.

[89] C.K. Larsen, Chloride binding in concrete, Dr. Ing. Thesis, Report No 1998:101, Norwegian University of Science and Technology, NTNU, 1998.

[90] H. Justnes, A review of chloride binding in cementitious systems, Nordic Concrete Research, Publication No. 21. 1/98, Nordic Concrete Federation, Norsk Betongforening, Oslo, 1998, pp. 48–63.

[91] L. Tang, L.-O. Nilsson, Chloride binding capacity and binding isotherms of OPC pastes and mortars, Cement and Concrete Research 23 (1993) 247–253.

[92] C.L. Page, Ø. Vennesland, Pore solution composition and chloride binding capacity of silica fume-cement pastes, Materials and Structures 19 (1983) 19–25.

[93] C. Arya, N.R. Buenfeld, J.B. Newman, Factors influencing chloride-binding in concrete, Cement and Concrete Research 20 (1990) 291–300.

[94] R.K. Dhir, M.R. Jones, Development of chloride-resisting concrete using fly ash, Fuel 78 (1999) 137–142.

[95] O.A. Kayyali, M.N. Haque, The Cl—/OH— ratio in chloride-contaminated concrete — a most important criterion, Magazine of Concrete Research 47 (1995) 235–242.

[96] S. Diamond, Effects of two danish flyashes on alkali contents of pore solutions of cement-flyash pastes, Cement and Concrete Research 11 (1981) 383–394.

[97] M. Kawamura, O.A. Kayyali, M.N. Haque, Effects of flyash on pore solution composition in calcium and sodium chloride-bearing mortars, Cement and Concrete Research 18 (1988) 763–773.

[98] R.K. Dhir, M.A.K. El-Mohr, T.D. Dyer, Chloride binding in GGBS concrete, Cement and Concrete Research 26 (1996) 1767–1773.

[99] R. Luo, Y.B. Cai, C.Y. Wang, X.M. Huang, Study of chloride binding and diffusion in GGBS concrete, Cement and Concrete Research 33 (2003) 1–7.

[100] A. Cheng, R. Huang, J.-K. Wu, C.-H. Chen, Influence of GGBS on durability and corrosion behavior of reinforced concrete, Materials Chemistry and Physics 93 (2005) 404–411.

[101] E. Mahallati, M. Saremi, An assessment on the mill scale effects on the electrochemical characteristics of steel bars in concrete under DC-polarization, Cement and Concrete Research 36 (2006) 1324–1329.

[102] J.A. González, E. Ramírez, A. Bautista, S. Feliu, The behaviour of pre-rusted steel in concrete, Cement and Concrete Research 26 (1996) 501–511.

[103] K. Tuutti, Effect of cement type and different additions on service life, in: Proc. Int. Conf. "Concrete 2000", Dundee, Scotland, UK, E & FN Spon, Chapman & Hall, London, 1993, pp. 1285–1295.

[104] J. Tritthart, Chloride binding in cement. II. The influence of the hydroxide concentration in the pore solution of hardened cement paste on chloride binding, Cement and Concrete Research 19 (1989) 683–691.

[105] C.M. Hansson, T. Frolund, J.B. Markussen, The effect of chloride cation type on the corrosion of steel in concrete by chloride salts, Cement and Concrete Research 15 (1985) 65–73.

[106] C.L. Page, N.R. Short, W.R. Holden, The influence of different cements on chloride-induced corrosion of reinforcing steel, Cement and Concrete Research 16 (1986) 79–86.

[107] Ø. Vennesland, C. Andrade, M.A. Climent, R. Polder, J. Gulikers, Recommendation of RILEM TC 178-TMC: "Testing and modeling chloride penetration in concrete": Method of field determination of critical chloride content which causes corrosion of reinfocement, draft.

[108] M. Stern, A.L. Geary, Electrochemical polarization. I. A theoretical analysis of the shape of polarization curves, Journal of the Electrochemical Society 104 (1957) 56–63.

[109] C. Andrade, C. Alonso, J. Gulikers, R. Polder, R. Cigna, Ø. Vennesland, M. Salta, A. Raharinaivo, B. Elsener, Recommendation of RILEM TC 154-EMC: "Test methods for on-site corrosion rate measurement of steel reinforcement in concrete by means of the polarization resistance method", Materials and Structures 37 (2004) 623–643.

[110] C. Alonso, C. Andrade, M. Castellote, P. Castro, Reply to the discussion by T.U. Mohammed and H. Hamada of the paper "Chloride threshold values to depassivate reinforcing bars embedded in a standardized OPC mortar", Cement and Concrete Research 31 (2001) 839–840.

[111] B.B. Hope, J.A. Page, A.K.C. Ip, Corrosion rates of steel in concrete, Cement and Concrete Research 16 (1986) 771–781.

[112] J.A. González, E. Otero, S. Feliu, W. López, Initial steps of corrosion in the steel/Ca$(OH)_2 + Cl^-$ system: the role of heterogeneities on the steel surface and oxygen supply, Cement and Concrete Research 23 (1993) 33–40.

[113] R.K. Dhir, M.R. Jones, H.E.H. Ahmed, Determination of total and soluble chlorides in concrete, Cement and Concrete Research 20 (1990) 579–590.

[114] M. Castellote, C. Andrade, Round–Robin test on chloride analysis in concrete — Part I: analysis of total chloride content, Materials and Structures 34 (2001) 532–556.

[115] R.S. Barneyback, S. Diamond, Expression and analysis of pore fluids from hardened cement pastes and mortars, Cement and Concrete Research 11 (1981) 279–285.

[116] J. Tritthart, Chloride binding in cement. I. Investigations to determine the composition of porewater in hardened cement, Cement and Concrete Research 19 (1989) 586–594.

[117] C. Arya, An assessment of four methods of determining the free chloride content of concrete, Materials and Structures 23 (1990) 319–330.

[118] G.K. Glass, Y. Wang, N.R. Buenfeld, An investigation of experimental methods used to determine free and total chloride contents, Cement and Concrete Research 26 (1996) 1443–1449.

[119] C. Arya, N.R. Buenfeld, J.B. Newman, Assessment of simple methods of determining the free chloride ion content of cement paste, Cement and Concrete Research 17 (1987) 907–918.

[120] M. Castellote, C. Alonso, C. Andrade, P. Castro, M. Echeverría, Alkaline leaching method for the determination of the chloride content in the aqueous phase of hardened cementitious materials, Cement and Concrete Research 31 (2001) 233–238.

[121] AASHTO T260, Standard method of test for sampling and testing for chloride ion in concrete and concrete raw materials, American Association of State Highway and Transportation Officials.

[122] B. Elsener, L. Zimmermann, H. Böhni, Non destructive determination of the free chloride content in cement based materials, Materials and Corrosion 54 (2003) 440–446.

[123] U. Angst, B. Elsener, C.K. Larsen, Ø. Vennesland, Potentiometric determination of the chloride ion activity in cement based materials, submitted to Journal of Applied Electrochemistry.