



Chloride threshold level for corrosion of steel in concrete

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Abstract

The steel rebar inside reinforce concrete structures is susceptible to corrosion when permeation of chloride from deicing salts or seawater results in the chloride content at the surface of the steel exceeding a chloride threshold level (CTL). The CTL is an important influence on the service life of concrete structures exposed to chloride environments. The present study discusses the state of art on the CTL for steel corrosion in concrete, concerning its measurement, representation, influencing factors and methods to enhance the CTL. As the CTL values reported in the majority of previous studies were varied with experimental conditions, corrosion initiation assessment method, the way in which the CTL was represented, direct comparison between the results from different sets and evaluation was subjected to the difficulty. As a result, total chloride by weight of cement or the ratio of $[\text{Cl}^-]:[\text{H}^+]$ is the best presentation of CTL in that these include the aggressiveness of chlorides (i.e. free and bound chlorides) and inhibitive nature of cement matrix. The key factor on CTL was found to be a physical condition of the steel–concrete interface, in terms of entrapped air void content, which is more dominant in CTL rather than chloride binding, buffering capacity of cement matrix or binders. The measures to raise the CTL values using corrosion inhibitor, coating of steel, and electrochemical treatment are also studied.

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1. Introduction

The importance of chloride ions in the corrosion of steel in concrete has led to the concept of a chloride threshold level (CTL). The CTL can be defined as the content of chloride at the steel depth that is necessary to sustain local passive film breakdown and hence initiate the corrosion process [1]. It is usually presented as the ratio of chloride to hydroxyl ions, the free chloride content or the percentage of the total chloride content relative to the weight of cement.

Assessment of the CTL is a key element in predicting the service life of structures exposed to chlorides. One possible definition of the service life is the time required for transport processes to raise the chloride level at the depth of the steel to the CTL. The first measurement of CTL was performed by Hausman [2] using a synthetic concrete solution with a $[\text{Cl}^-]:[\text{OH}^-]$ ratio of 0.6. The CTL measured for bridges in the UK ranges from 0.2 to 1.5% by weight of cement, when expressed as total chloride [3]; the British Standard [4] limits the chloride content to less than 0.4% for reinforced concrete structures and 0.1% for prestressed concrete structures. However, CTL in free chloride content alone has rarely been measured, compared to total chloride content or the ratio of $[\text{Cl}^-]:[\text{OH}^-]$.

Despite the importance of the CTL, conservative values such as 0.2% or 0.4% by weight of cement have been used in predicting the corrosion-free life, because of the uncertainty regarding the actual limits in various environments for chloride-induced corrosion [5–9].

A considerable amount of research has focused on quantifying the CTL for steel corrosion, but the measured values cover an extremely wide range. The reasons for the wide range of reported CTL include the method of measurement, method of presentation of CTL, condition of the steel–concrete interface and the influence of environmental factors. For example, the assessment of the CTL using a solution to replicate concrete produces errors when applied to steel in hardened concrete. The present study concerns the methods of measuring the CTL, including its representation, influencing factors as well as to raise the CTL.

2. Measurement

2.1. Corrosion initiation

To measure the CTL, the time of onset of corrosion and the chloride content at the steel depth must be identified. The onset of corrosion can be detected by monitoring the macrocell current between an anode and a cathode, measuring half-cell potential or monitoring the corrosion rate measured by the polarisation technique or AC impedance method.

Macrocell devices are widely used (ladder systems are common) to monitor the risk of reinforcement corrosion, with corrosion initiation shown by a sharp increase in the macrocell current. A macrocell consists of steel anodes and a single, nobler cathode usually made from titanium mesh, graphite or stainless steel; in practice, the whole macrocell is embedded in the concrete cover above the reinforcement. The measured macrocell current, however, does not provide a direct corrosion rate reading, and may give an incorrect reading in dry concrete conditions.

Half-cell potential measurement is probably the most common method used for measuring the risk of reinforcement corrosion [10–12]. In practice, the potential is measured at various points on the concrete surface on a grid pattern relative to the reinforcement

and a potential map plotted. Areas of high potential are indicative of a greater risk of reinforcement corrosion. The method, however, is often inconclusive because it depends on the condition of the concrete such as moisture level, the amount of carbonation and salt concentration, which will affect the reading and can lead to an erroneous judgment.

Measurement of the corrosion rate by electrochemical polarisation or AC impedance methods gives the most accurate information on corrosion. These methods provide a direct reading of corrosion rate, but the relationship between corrosion rate and the onset of corrosion is not clear-cut and can vary over a wide range, in turn affecting the precision of the CTL. The corrosion rate of reinforcing steel is often regarded as being significant when it exceeds 1–2 mA/m² [13]. Uncertainty surrounds depassivation, however, which cannot be detected by visual observation because it may take some time for the coloured oxides resulting from corrosion to appear.

Mass loss of steel bar due to corrosion, although not giving the time to corrosion, can also be used to determine the CTL [3,14,15]. The mass loss is calculated by weighing the bar before installation in concrete, then removing it after a set time, cleaning off the rust and re-weighing. The method is only applicable where a significant amount of visible corrosion has occurred. It does not indicate pitting corrosion where little mass loss occurs. Table 1 shows methods used for detecting the onset of corrosion, as well as the CTL inferred from published data.

2.2. Chloride content

Measurement of the chloride content or profile to determine the CTL is performed after corrosion initiation. There are two stages in measuring the chloride content: sampling and analysis. Sampling generally involves grinding the concrete and collecting dust at various depths. It is essential to ensure that there is an approximately equal portion of cement paste in each sample, compared to a bulk concrete, as there is a risk of the sample being dominated by large aggregate sizes.

The free (water soluble) chloride concentration is measured from a solution obtained by boiling the extracted dust concrete/mortar sample in water [16]. The concentration of chloride can be determined using potentiometry or a chloride ion sensitive electrode; the chloride concentration is expressed as percentage of the weight of cement or concrete. Water soluble chloride measured by water extraction is dependent on the fineness of the pulverised sample, amount of added water, temperature, agitation method and time allowed for extraction [17]. The pore press method involves extracting the pore solution from the cement paste under high pressure, and is more accurate than the water extraction method [18]. However, in this procedure, bound chlorides may be freed so that the free chloride content can be overestimated [19,20].

The most widely adopted method for measuring total chloride content uses acid soluble extraction, in which it is assumed that both bound and free chlorides are soluble in acid. Measurement of acid soluble chloride (total chloride) may be made using a chloride ion sensitive electrode or by titration, for example as described in British Standard 1881 Part 124 [21].

X-ray fluorescence can also be used to determine the chloride content [22,23]. However, the equipment is costly and requires a high level of expertise to operate, and for these reasons its use is confined to specialist laboratories.

Table 1
Chloride threshold level reported by various authors with varying conditions

Condition	Threshold values			Detection method	Reference
	Total chloride (% , cem.)	Free chloride (% , cem.)	$[\text{Cl}^-]/[\text{OH}^-]$		
Pore solution			0.6	Half-cell potential	[2]
			0.3	Polarisation	[33]
Specimen + internal Cl^-			8–63	Polarisation	[34]
	0.5–2.0			Macrocell current	[1]
	0.079–0.19			AC impedance	[81]
	0.32–1.9			Mass loss	[14]
	0.78–0.93	0.11–0.12	0.16–0.26	Half-cell potential	[12]
	0.45 (SRPC)	0.10	0.27		
	0.90 (15% PFA)	0.11	0.19		
	0.68 (30% PFA)	0.07	0.21		
	0.97 (30% GGBS)	0.03	0.23		
		0.35–1.00	0.14–0.22		$\text{Cl}^-/\text{OH}^- = 0.3$
Specimen + external Cl^-	0.227	0.364	1.5	Polarisation	[28]
	0.5–1.5			Half-cell potential	[11]
	0.70 (OPC)			Mass loss	[15]
	0.65 (15% PFA)				
	0.50 (30% PFA)				
	0.20 (50% PFA)				
	1.8–2.9			Polarisation	[26]
	0.5–1.4			Not mentioned	[25]
	0.6–1.4			Macrocell	[50]
Structure	0.2–1.5			Mass loss	[3]

Note: SRPC: sulphate resistant Portland cement, PFA: pulverised fly ash, GGBS: ground granulated blast furnace slag, OPC: ordinary Portland cement.

3. Representations

3.1. Free chloride content

The representation of CTL reflects the aggressive ion content and inhibitive properties of the cement matrix. Chloride ions which are removed from the pore solution as the result of an interaction with the solid matrix (bound chloride) are relatively immobile and may not be transported to the steel surface. This should in theory favour the use of the free chloride content (water soluble chloride) to represent the CTL [24,25]. Results by Pettersson [26] show a wide range of the CTL values in terms of free chloride concentration, ranging from 0.28 to 1.8 M in mortar specimens with water/cement ratios between 0.3 and 0.75. More recent works by Alonso et al. [27,28] reported CTL values in terms of free chloride content by weight of cement, ranging from 0.3% to 2.0%.

Early works suggested that only the free chloride contributes to the corrosion process [29] and hence the free chloride content was regarded as the best expression of this. This proposals have been challenged by current thinking, when considering that (1) bound chlorides at the steel depth are released to form free chlorides when the pH drops due to depassivation [30], and (2) cement hydration products such as calcium hydroxide resist a fall in pH at a particular value of the pH [31,32]. It should be noted that current guidelines and standards do not address the free chloride content in relation to corrosion risk, largely for the reasons mentioned above. The free chloride content is more often expressed as a function of hydroxyl ion concentration in the pore solution, or the mole ratio of chloride to hydroxyl ions.

3.2. $[Cl^-]:[OH^-]$

This approach assumes that bound chlorides are not a risk to corrosion, and that the hydroxyl ion concentration reflects the inhibitor content of the environment by sustaining the high pH of the pore solution. In early works, the relation between free chloride and hydroxyl concentration was used to express the CTL in terms of the ratio of free chloride to hydroxyl concentration [2,33]. This expression of the CTL is still currently used [27,34–37]. A threshold ratio varying from 0.3 to 40.0, as given in Table 1, was reported.

Expressing CTL as the $[Cl^-]:[OH^-]$ ratio implies that the hydroxyl ion concentration reflects the inhibitor content of the environment; it indicates the ratio of aggressive to inhibitive ions causing corrosion initiation in a solution environment. Gouda [33] described the relationship between chloride and hydroxyl ions by the following equation.

$$pH = n \log[Cl^-] + K$$

where n and K are constants. This implies that the ratio $[Cl^-]^n:[OH^-]$ represents a constant with $n \approx 0.8$ for corrosion prevention.

The ratio of $[Cl^-]:[OH^-]$ has been considered functional, because it reflects the corrosion risk that is induced by either chloride alone, or carbonation and chloride in combination. Carbonation helps release the bound chloride, thereby increasing the concentration of free chloride as the pore solution pH falls. As a result, the ratio of chloride to hydroxyl

concentration increases significantly and the threshold ratio may exceed the CTL, which indicates a higher corrosion risk.

The ratio of $[\text{Cl}^-]:[\text{OH}^-]$, however, may not represent the CTL well since it ignores the inhibitive effect of the cement matrix, which may include a relatively denser hydration product layer on the steel surface. Precipitated calcium hydroxide forms a continuous layer which prevents the pH from falling below 12.6 [38]. This can be confirmed if the ratio measured is not different between solution and concrete. As seen in Table 1, the ratio determined in the simulated pore solution ranges from 0.25 to 1.0, whereas the threshold ratio expressed in mortar specimens is higher and varies more widely, ranging from 1 to 40.

Moreover, the ratio of $[\text{Cl}^-]:[\text{OH}^-]$ does not consider the dependence of chloride binding capacity on the hydroxyl concentration. The alkaline environment within concrete is caused primarily by the presence of metal hydroxides (KOH or NaOH). An investigation carried out by Page and Treadaway [38] indicated that the pore solution is more likely to be in the pH range 13–14, rather than 12.6. This is due to the fact that pore fluid consists of NaOH and KOH in addition to $\text{Ca}(\text{OH})_2$ solution (pH 12.6). The reduction of alkalinity may destabilise the chloro aluminate, thus releasing chloride into the pore solution. However, an increase in the pH above 12.6 has been observed to produce a remarkable decrease in the level of the bound chloride [39,40]. An analysis of the data by Tritthart [39], as given in Fig. 1, showed that an increase in the pH is accompanied by an increase in the $[\text{Cl}^-]:[\text{OH}^-]$ ratio at a fixed level of total chloride. This means that an increase in corrosion risk accompanies an increase in hydroxyl ions, in spite of the inhibitive effect of hydroxyl ion.

3.3. Total chloride

The representation of the CTL by the total chloride level is the most widely used approach, and is the approach adopted in standards [4,41–43]. Table 2 gives the limit of the total chloride content of concrete from each standard.

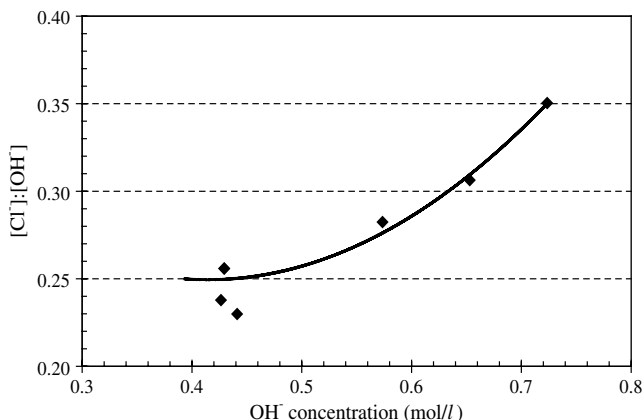


Fig. 1. Effect of pH on chloride binding at a fixed level of total chloride (1% by weight of cement) adding chloride as HCl, MgCl_2 and CaCl_2 ; based on the data of Ref. [39].

Table 2
Maximum chloride content values set by various ACI and BS documents

Type	Maximum chloride content (% of cement)			
	BS 8110	ACI 201	ACI 307	ACI 222
Prestressed concrete	0.10		0.06	0.08
Reinforced concrete exposed to chloride in service	0.20	0.10	0.10	0.20
Reinforced concrete that will be dry or protected from moisture in service	0.40			
Other reinforced concrete		0.15		

The representation of the CTL as the total chloride content as a percentage by weight of cement, is favoured because it is relatively easy to determine and because it involves the corrosion risk of bound chloride and the inhibitive effect of cement hydration products. At the stage of corrosion initiation, the pH in the vicinity of the steel falls locally as a result of an electrochemical reaction with chloride and ferrous ions during pit nucleation. Corrosion is initiated in the form of pitting where the local pH falls below 10. The drop in pH releases at least 90% of the total surrounding chloride ions to participate in the corrosion process [30,31,44] with access to oxygen and water as well as chloride accelerating the rate of corrosion. This suggests that the total chloride content is a more accurate indicator of corrosion risk and the inhibitive nature of cement may thus be better reflected by the total cement content rather than the pore solution pH. Hence, the total chloride content to cement weight is the better representation of the CTL because (1) the inhibitive properties of cement matrix are reflected by its cement content and (2) the total aggressive potential of chloride ions is represented.

As seen in Table 1, the wide range of CTL values reported in terms of the total chloride content is due to a number of factors. The importance of individual factors is not always clear and no work has successfully modelled the variation in CTL as a function of a single parameter.

3.4. $[Cl^-]:[H^+]$

In a recent work, it was suggested that a more appropriate representation of the inhibitive and aggressive properties of concrete is provided, respectively, by its acid neutralisation capacity (ANC) and acid soluble chloride content [31,45]. The acid neutralisation capacity has been used to quantify the buffering capacity of concrete. The content of acid needed to reduce the pH of concrete and cement paste suspended in water, up to a particular value, has been reported by Sergi and Glass [45]. The acid (moles H^+ /kg binder) required to reduce the pH to 10 was determined as 18.9, 17.5, 15.4 and 14.5 mol/kg for OPC, sulfate resisting Portland cement (SRPC), 30% pulverized fly ash (PFA) and 65% ground granulated blast furnace slag (GGBS), respectively. Thomas [15] determined the CTL of OPC and 30% PFA content as 0.7% and 0.5% by weight of cement, respectively. Based on these data, the CTL for OPC and 30% PFA equate to the same mole ratio of 0.01 $[Cl^-]:[H^+]$. A mole ratio of 0.01 also approximates to 0.65% and 0.5% chloride by weight of cement in SRPC and 65% GGBS concretes, respectively. The ratio of total chloride to ANC is probably the best representation of the CTL, since it considers all potentially important inhibitive (cement hydration products) and aggressive (total chloride) factors.

4. Influencing factors

4.1. Chloride binding

It is well known that C_3A and C_4AF bind chlorides to form $3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$ (Friedel's salt) and $3CaO \cdot Fe_2O_3 \cdot CaCl_2 \cdot 10H_2O$, respectively. Chloride binding can be defined as the interaction between the cement matrix and chloride ions, which results in the removal of chlorides from the pore solution [46]. Binding capacity has been regarded as important in the corrosion of steel in concrete structures because of the conventional view that chemically bound chlorides do not participate in the corrosion process [47]. Hence, it has been thought that a higher binding capacity is associated with less corrosion risk.

Several investigations have addressed the influence of the chloride binding capacity on the CTL, particularly in terms of the C_3A content. Hussain et al. [48] found that the CTL increased with C_3A content; three plain cements with C_3A contents of 2.43%, 7.59% and 14% were tested and CTL values for those cements were 0.35%, 0.62% and 1.00%, respectively, as the time to corrosion was determined using $[Cl^-]:[OH^-]$ ratio to reach 0.3. The strong relationship shown between the CTL and C_3A content is supported by corrosion potential monitoring which found that OPC concrete with 11.2% of C_3A produced a CTL of >1% by weight of cement, while SRPC with 1.41% C_3A lowered the CTL [49].

On the other hand, concrete specimens made from cement with a low proportion of C_3A , such as SRPC, do not always show a lower CTL when the corrosion state is monitored with a macrocell. Analysis of the CTL obtained by Hansson and Sorenson [50] shows no correlation between the CTL and chloride binding capacity. Breit and Schiessl [51] reported similar CTL values for OPC and SRPC concretes, ranging from 0.2% to 0.4%. This suggests that chloride binding capacity has less influence on the CTL for a sustained corrosion process, possibly due to the participation of bound chloride in the corrosion initiation process [31].

The influence of the binding capacity on the CTL is unclear; one possible reason may be the inaccuracy of the methods used to detect the onset of corrosion. The half-cell potential monitoring for corrosion is complicated by other variables affecting the corrosion potential (see Table 1), and the time for threshold ratio of $[Cl^-]:[OH^-]$ to reach 0.3, obtained from a beaker test, may not be applicable to judge the corrosion initiation.

Despite the uncertainty concerning the effect of chloride binding on the CTL, chloride binding does reduce chloride transport in concrete and lower corrosion rate. Also, chloride binding affects the chloride transport by immobilising a portion of chloride ions [52]. The corrosion rate for SRPC concrete (which has less chloride binding) is much higher than for OPC concrete because of the higher free chloride levels [53].

4.2. Buffering capacity

The pH dependent dissolution behaviour of cement hydration products can be determined from ANC testing which measures the resistance to a fall in pH. In this method, the titration curve (pH against molar equivalent of acid) shows several plateaus (in spite of a continuous supply of acid), representing the inhibitive effect arising from the resistance of different cement hydration products to a pH reduction. One of the peaks, occurring at about pH 12.6, represents the buffering of calcium hydroxide [54].

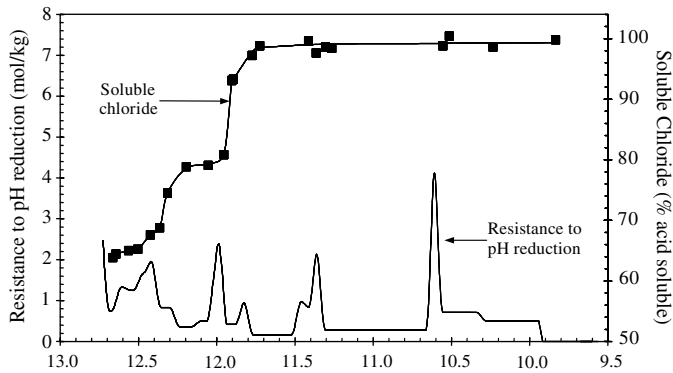


Fig. 2. pH dependent release of chloride and ANC analysis plot obtained from chloride-contaminated OPC concrete [31].

Glass et al. [31] performed the ANC test on chloride contaminated concrete specimens and also measured the change in free chloride content as the pH was decreased. Fig. 2 gives the pH dependent release of chloride and ANC analysis plot [31]. It is evident that most of the bound chloride is released as the result of dissolution of several hydration phases. Since the pH value is about 10 at the stage of corrosion initiation, it can be said that the bound chloride released by such a local pH reduction may also participate in corrosion initiation. This hypothesis is supported by Reddy [44] who reported that SRPC has similar values of CTL to those of OPC, 30% PFA or 65% GGBS concretes at a given interfacial air void content, while a mixture of OPC and calcium aluminate cement (CAC), associated with a high level of ANC, has a much higher CTL. Table 3 gives the buffering capacity up to pH 10, measured by the ANC tests, of OPC, 30% PFA, 65% GGBS, SRPC and 10% CAC concretes.

However, the measured CTL tends to be different for specimens cast from the same concrete mix (same binding capacity and same ANC value). This can be attributed to other factors, which may include the condition of the steel–concrete interface.

4.3. Steel–concrete interface

When concrete is cast against a steel bar, a dense continuous cement rich layer containing precipitated calcium hydroxide is postulated to be formed at the steel–concrete

Table 3
Buffering capacity of binders as measured by the ANC method [44]

ANC (mol/kg)				CTL (% , cement)
	pH 12	11	10	
OPC	1.05	1.75	2.25	0.23–1.52
10% CAC	0.83	1.87	2.26	0.72–2.35
SRPC	0.92	1.26	2.08	0.31–0.53
30% PFA	0.51	1.23	1.8	0.25–0.35
65% GGBS	0.41	1.31	1.73	0.22–0.51

Note: OPC: ordinary Portland cement, CAC: calcium aluminate cement, SRPC: sulphate resistant Portland cement, PFA: pulverised fly ash, GGBS: ground granulated blast furnace slag.

interface [55]. This layer restricts the tendency for a decrease in pH to occur at anodic areas and reduces the mobility of chloride ions [38]. Suryavanshi et al. [36] supported this hypothesis; they found that steel taken from a mortar specimen was covered with a thin, dense white-deposit approximately 10–15 μm in thickness, which showed a strong Ca peak in the EDX spectrum. The characteristics of the interfacial layer depend mainly on the characteristics of hydrated cement paste which consists of solids and pores. The solids in cement paste consist of C–S–H gel (50–60%), $\text{Ca}(\text{OH})_2$ (20–25%), AFm and Aft (15–20%), and unhydrated clinker grains [56].

However, Glass et al. [57] examined the steel–concrete interface in backscattered electron (BSE) microscopy and observed no continuous $\text{Ca}(\text{OH})_2$ layer at the steel–concrete interface. It was subsequently found that 5–9% of calcium hydroxide occupies the steel–concrete interface region (area within 10 μm from the steel surface), while the coarse porosity accounts for approximately 30% of the cement paste in this region, as shown in Fig. 3 [58].

The importance of entrapped air voids adjacent to the embedded steel has been emphasised, because corrosion starts there. Air voids are often generated by bleeding or/and settlement underneath the embedded steel, perpendicular to the direction of casting, and then corrosion initiates in these voids irrespective of whether chlorides are introduced internally or externally [59–61]. This is due to the fact that voids, in the vicinity of the steel, saturated in pore solution, provide a more active environment for electrochemical reactions (i.e. corrosion) than the dense cement matrix which relatively restricts current flow between anode and cathode. It is now established that air voids at the steel–concrete interface have a significant effect on the CTL. This effect is attributed to the absence of cement hydration products at these locations that would otherwise resist a local fall in the pH. The

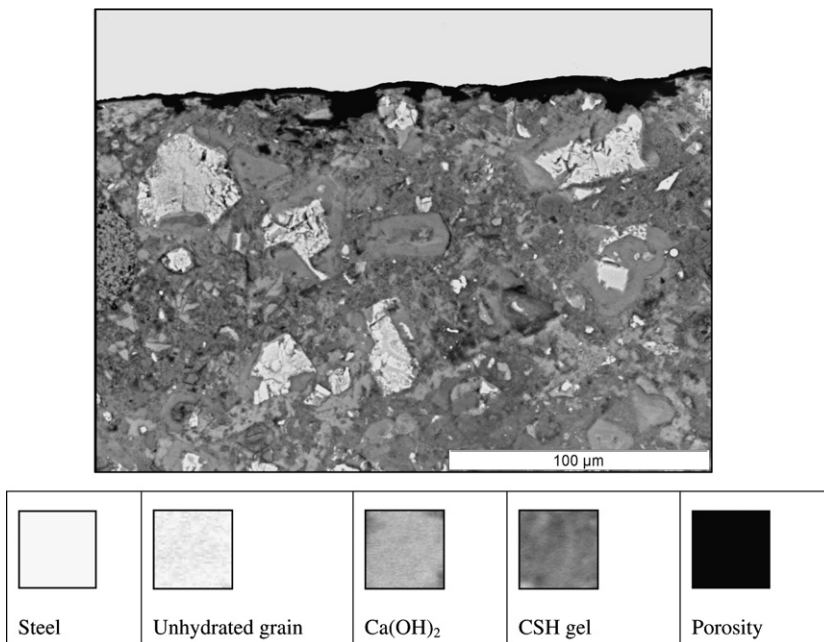


Fig. 3. Backscattered electron image at the steel–concrete interface [58].

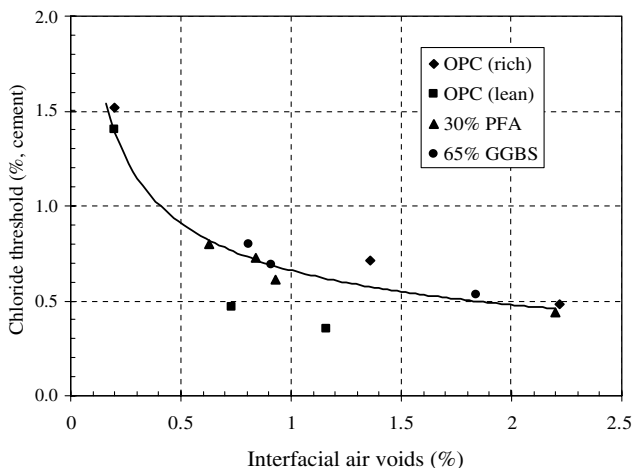


Fig. 4. Relationship between the air void content at the steel–concrete interface and the CTL for OPC, 30% PFA and 65% GGBS concretes [58].

importance of voids at the interface on the CTL is supported experimentally by Yonezawa et al. [34] who showed strong correlation between the interface condition (i.e. adhesion to mortar) and the CTL. However, the conclusion in this work was based on data obtained on a limited number of mortar specimens with cast-in chloride. More currently it was found that an increase in the air void content resulted in a sharp decrease in CTL as seen in Fig. 4 [58].

Although the physical condition of the steel–concrete interface in terms of the entrapped air void content has an effect on the CTL, quantification of the effect of voids at the interface has seldom been reported. One of the reasons for this is the difficulty of measuring the air void content at the interface non-destructively. Glass and Buenfeld [62] achieved some success in measuring the air voids at the steel–concrete interface with an ultrasonic method. However, this technique was only applicable to larger voids and the presence of a ribbed bar limited the detection.

4.4. Cement replacement

The effect of cement replacement on the CTL has received little coverage in the literature, in contrast to the widely reported assessment of its effect on chloride diffusion, the possible reason being the much longer time to corrosion initiation for PFA and GGBS concretes, which are very resistant to chloride transport. Fig. 5 shows reported CTLs for PFA and GGBS concretes depending on their replacement content and chloride source (i.e. internally admixed or external chlorides).

Thomas [15] showed that an increase in the content of PFA in concrete exposed to seawater produced a decrease in the CTL. However, the mass loss of the steel embedded in PFA concrete measured at 4 years decreased as the content of PFA increased. Thomas and Matthews [63] subsequently reported a reduction in the CTL of PFA concrete based on 10-year performance of PFA concrete, including chloride transport and corrosion of embedded steel, both of which were reduced by PFA replacement. They also showed that

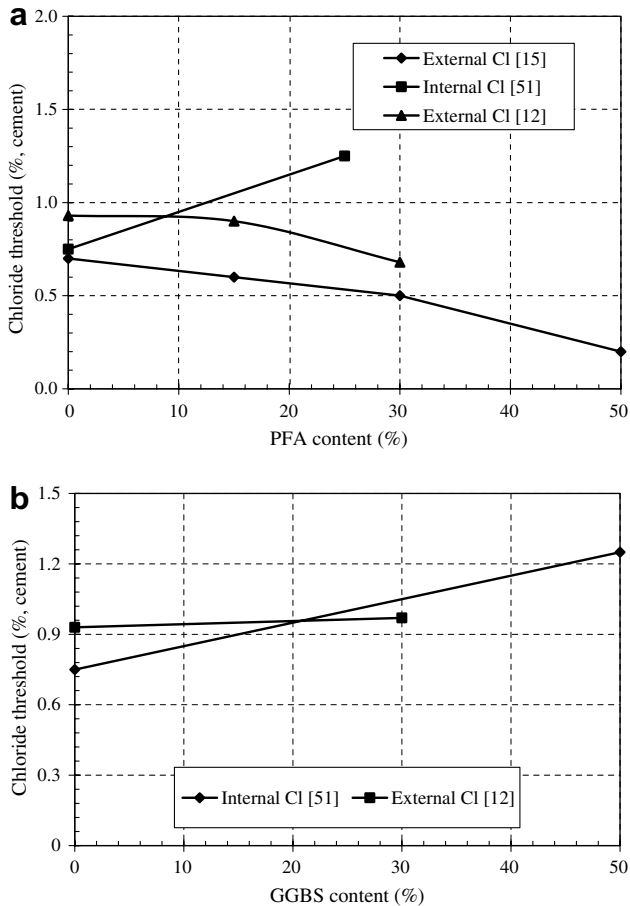


Fig. 5. CTL of (a) PFA and (b) GGBS concrete with internal and external chloride.

the time to corrosion can be prolonged and corrosion propagation restricted by the addition of PFA, despite a lower CTL. Similarly, Oh et al. [12] found that an increase in the PFA content from 15% to 30% resulted in a decrease in the CTL from 0.90% to 0.67%, using half-cell monitoring to judge corrosion initiation. In contrast, it was reported that the CTL for PFA concrete was higher than that for OPC, when the chloride was introduced in the mixing water and the macrocell current was monitored for 300 days [51]. The CTL for 25% PFA concrete ranged from 1.0% to 1.5%, while OPC produced a CTL of 0.5–1.0%. PFA replacement decreased the CTL except for the results from Breit and Schiessl [51]. The decreased CTL for PFA concretes may be ascribed to the low buffering capacity of PFA cement matrix. The lowered chloride buffering capacity of PFA concrete, which is about 48–80% compared to OPC concrete (see Table 3), may result in more free chlorides in the pore solution at corrosion initiation and hence increase the risk of corrosion. However, the reason for the increased CTL for PFA concrete in the case of internally admixed chloride and macrocell current monitoring is not fully understood. This discrepancy on the influence of PFA on CTL may arise from there being other more

dominant factors such as physical condition of the steel–concrete interface. It seems that the CTL may be dependent on the external environmental factors, the chloride source and the corrosion detection method.

When chloride ions were allowed to penetrate concrete from an external source, Oh et al. [12] obtained a marginal influence of GGBS on CTL: the CTL for 30% GGBS was 0.97% by weight of cement, while the CTL for OPC concrete was 0.93%. Breit and Schiessl [51] reported that the CTL for GGBS concrete was higher than that for OPC, when the chloride was admixed in the mixing water. The CTL for 50% GGBS concrete ranged from 1.0% to 1.5%, while OPC produced a CTL of 0.5% to 1.0%. The increase in CTL due to GGBS replacement may be due to the higher binding capacity of GGBS with its high aluminate levels [64,65].

Notwithstanding debate over the effect of cement replacement on the CTL, PFA and GGBS concrete are beneficial in delaying the time to corrosion for an external chloride source. This is supported by Hussain and Rasheeduzafar [10], who compared the time to corrosion for OPC and 30% PFA concretes. The time to corrosion for 30% PFA concrete was 400 days, compared to OPC concrete which allowed corrosion after 214 days, when specimens were immersed in NaCl solution. Bamforth [11] also showed that steel remained passive in PFA and GGBS concretes when exposed to a marine atmosphere for eight years, whereas the steel corroded in OPC concrete. Dehwah et al. [66] showed that PFA increased the time to corrosion, when specimens were exposed to a 5% NaCl solution. The increased time to corrosion for PFA or GGBS concrete generally arises from a reduction of chloride transport due to (1) a refinement of pore structure, and (2) the increased binding capacity of GGBS.

4.5. Other factors

External environmental factors such as relative humidity, temperature, moisture level and type of cation have also been reported to influence the CTL. Hussain et al. [48] indicated that exposure temperature has a very strong influence on the CTL. An increase in temperature from 20 to 70 °C caused a 5-fold reduction in the CTL. Also, an increase in temperature lowered the percentage of bound chloride and reduced the pore solution pH.

The CTL also depends on the moisture level in the concrete, because the moisture level affects the mobility of chloride ions, the potential of the environment and the chloride concentration in the pore solution. When oxygen is not restricted, higher moisture contents are reported to decrease the CTL [26]. This may be due to a decrease in the resistivity of concrete. However, controlling these external factors is almost impossible in most practical applications.

The effect of resistivity has been little investigated in spite of the significant effect it has on the CTL. Morris et al. [67] showed that an increase in resistivity from 2 to 100 k Ω -cm resulted in an increase in CTL from 0.44% to 2.32%, when measuring the resistivity between two rebars in concrete using Nilsson 400 soil resistivity meter.

The potential and composition of embedded steel in concrete may influence the CTL. An increase in the proportion of nickel and/or chromium may have an inhibitive effect. Normal mild steel with 0.18–0.55% of nickel and chromium had CTL values ranging from 0.04% to 0.09%, while the CTL of steels with high nickel and chromium levels of 0.82% and 1.91% varied from 8.64% to 10.8% and from 10% to 18%, respectively, [68,69]. This

effect is mainly due to the shift in potential in the noble direction, making the steel more resistant to chloride-induced corrosion. It has been shown that a change in cathodic potential by means of an impressed DC current increases the CTL [28].

5. Raising threshold values

5.1. Corrosion inhibitors

The advantage of using corrosion inhibitors to provide corrosion protection is that the inhibitor is well distributed throughout the concrete, which means that it protects all the steel. A corrosion inhibitor modifies the surface chemistry of steel to mitigate or prevent the corrosion process. While numerous corrosion inhibitors have been suggested, the detrimental effects of many of them in concrete limit their commercial use [70].

Calcium nitrite has been widely used as a corrosion inhibitor in concrete since the middle of the 1970s, because of its inhibiting effect as well as its compatibility with concrete [71,72]. It enhances the compressive strength at an early age, and accelerates the setting time within the range recommended by standards [73].

A number of works have shown that calcium nitrite is very effective in mitigating chloride-induced corrosion in concrete, reducing the corrosion rate and potential and also significantly increasing the time to corrosion [74–78]. However, the use of good quality concrete is advised in order to enhance the inhibiting effect of calcium nitrite. Gaidis et al. [79] showed that the use of calcium nitrite in high-strength concrete raised the inhibiting effect in two probe potential tests and more recently Montes et al. [80] also showed that a low water–cement ratio and replacement with PFA increases the inhibition effect.

The CTL has been mostly presented as the mole ratio of $[\text{NO}_2^-] : [\text{Cl}^-]$ when calcium nitrite has been used, because it indicates the amount of corrosion inhibitor required to inhibit chloride-induced corrosion. Hope and Ip [81] suggested that a $[\text{NO}_2^-] : [\text{Cl}^-]$ ratio of 0.07–0.09 was necessary to inhibit steel corrosion in a concrete pore solution. For concrete, the inhibitive efficiency of nitrite is often considered to be in the range 0.5–1.0, as a mole ratio of nitrite to chloride ions [82–84]. Gonzalez et al. [85] also reported that the threshold ratio of nitrite to chloride is about 0.75–1.0, depending on the ratio of sand in mortar and curing condition, when sodium nitrite is used as a corrosion inhibitor. These studies, based on experimental results, indicate that an increase in the dosage of nitrite results in an increase in the chloride content needed to initiate corrosion.

However, a series of investigation on calcium nitrite recently found that calcium nitrite did not significantly affect the CTL in the beaker experiment using synthetic pore solution [86], in spite of the fact that the time to corrosion was delayed in mortar [87]. Also, surface tomography by the same authors suggests that any inhibiting effect may result from an increase in the electrolytic resistance of concrete using calcium nitrite, rather than a modification in the chemistry of the steel surface. Moreover, it was currently found that nitrite ions present in concrete may accelerate chloride transport and thus it was less effective in prolonging the time to corrosion despite the increased CTL [88].

5.2. Coating of reinforcing steel

Galvanisation. A galvanised (zinc) coating acts both as a sacrificial coating in protecting steel. It is reported in laboratory and field studies that galvanising increases the CTL.

Treadaway et al. [89] showed that galvanised steel in a concrete structure exposed to corrosive conditions delayed the initiation of corrosion and resulted in a CTL of 0.9% by weight of cement. The results of the monitoring of concrete structures in seaside environments over an 8–23 year period suggested a CTL of 0.64% when using galvanised steel, while untreated steel showed a CTL of 0.2% [90]. Bautista and Gonzalez [91] found that the corrosion rate for galvanised steels was much lower than that for bare steel; the corrosion rate for galvanised steel ranged from 0.2 to 1.2 $\mu\text{A}/\text{cm}^2$, while for bare steel it ranged from 0.4 to 10 $\mu\text{A}/\text{cm}^2$ after 12 months exposure to a chloride solution. The inhibiting effect of galvanising appears to be enhanced in high-performance concrete, with the time to corrosion considerably delayed [92].

Although documented evidence for the good protective properties of galvanised steel has been reported, there is controversy regarding its durability. Electrochemical studies show that hydrogen is evolved when a zinc coating is subjected to aqueous hydroxide environments, which results in a weakening of the bond strength between the steel and concrete. However, this problem has been solved by adding a small amount of chromate to the cement, which depresses the zincate–hydrogen reaction [93]. Kayyali and Yeomans [94] opposed the use of chromate, because they found no evidence of a long term reduction in bond strength due to the possible effects of hydrogen gas evolution resulting from the reaction between the zinc and wet concrete. Their experimental work shows an increase in bond of 2–24% for galvanised steel relative to untreated steel, without the addition of chromate. In spite of good performance results, little quantitative work of the effect of galvanised steel on the CTL has been reported.

Barrier coating. The corrosion of reinforcement in concrete can be prevented by coating the steel with epoxy, which stops aggressive ions reaching the steel surface. Care is required in the handling, transporting, storing and placing of epoxy-coated steel since damage can impair its corrosion protection performance. Erdogdu et al. [95] showed that the corrosion rate of coated steel bars was below 0.01 mA/m^2 after 25 months exposure, compared to 2–100 mA/m^2 for uncoated steel bars after 5 months exposure. Al-Amoudi et al. [96] showed the effect on CTL of epoxy-coated steel with various degrees of coating damage. With 1% damage to the coating, the CTL was about 2% by weight of cement, while at 2% damage, the CTL was below 0.4%.

The performance of epoxy-coated steel varies according to the application. Severe corrosion was reported after only 6 years service, in the case of epoxy-coated steel bars used in the substructure of bridges in the Florida Keys [97,98]. The cause of the problem may be disbondment between the coating and steel or poor installation that leads to defects and hence pitting corrosion. The flaws in the coating and its disbondment from the steel may be attributed to the bending of the coated steel during fabrication or exposure to a chloride environment before casting of the concrete [99]. A reduction in bond strength from 20% to 36% between epoxy-coated steel and concrete in ribbed steels, which is proportional to the thickness of the coating, has been reported [100–102].

Recent studies have shown that epoxy-coated steel can give good, long term performance even on severe exposure to chloride conditions and considering the effects of bond loss when properly coated and handled [95,103,104]. Cement-based coatings rather than resin coatings have been suggested because they perform better due to the higher bond strength as well as corrosion protection [105].

6. Conclusion

The present study reviewed concerning the chloride threshold level (CTL), and revealed the following conclusions, with respect to CTL representation, influencing factors, and methods to raise the CTL.

- The CTL value depends on how it is expressed, such as the mole ratio of $[\text{Cl}^-]:[\text{OH}^-]$, free chloride, or total chloride. The CTL has been expressed as free chloride or $[\text{Cl}^-]:[\text{OH}^-]$ in many previous studies, as being very widely ranged. The free chloride content or $[\text{Cl}^-]:[\text{OH}^-]$ has the disadvantage of poor accuracy and repeatability. It fails to consider the participation of bound chloride in sustained corrosion and the buffering capacity of the cement matrix.

The representation most widely used for the CTL is total chloride content relative to the cement weight, as it takes into account the inhibiting effect of cement and the aggressive nature of chloride and is convenient. CTL values in total chloride content are within a relatively narrow range, compared to values expressed in free chloride or $[\text{Cl}^-]:[\text{OH}^-]$.

The mole ratio of total chloride to the acid neutralisation capacity of cement (expressed as the mole concentration of H^+) has been proposed as a better method of capturing the inhibiting effect.

- The corrosion of steel is initiated at defects at the steel–concrete interface, commonly at entrapped air voids where there is an absence of cement hydration products. Hence, an increase in the air voids content at the interface leads to a greater probability of a lower CTL. The majority of previous studies of CTL have investigated the influence of binder type, in particular C_3A content. This has not resulted in a more precise definition because bound chloride is freed when there is a local fall in pH.

The influence of replacement materials, in particular pulverised fly ash and ground granulated blast furnace slag on the CTL is subject to debate. The CTL for concrete containing pozzolanic materials depends on whether the chlorides are introduced from an external environment or from the concrete constituents, and/or detecting on the method of corrosion initiation.

- Calcium-nitrite based corrosion inhibitors have been successfully applied to concrete structures for enhancing the resistance to chloride-induced corrosion. Calcium nitrite, in general, remarkably raised the CTL, and thus a much longer time to corrosion is expected. However, nitrite ions present in concrete allow external chlorides to more easily penetrate concrete, thereby offsetting the effect of increased CTL in prolonging the service life of structures.

Galvanisation and barrier coating have been used to protect the embedded steel in concrete from chloride or carbonation attack. However, their defect at the steel–concrete interface (i.e. a reduction of bond), which may be attributed to hydrogen evolution or smooth surface of coating, restricts the use in concrete structures.

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