Factors affecting the chloride threshold level for steel corrosion in concrete

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ABSTRACT

The present study surveys the concrete properties-concerned factors influencing the chloride threshold level for steel corrosion in concrete, altogether with supporting experimental works, in particular, chloride binding capacity, buffering capacity, condition of steel-concrete interface and cement replacement. It concluded that the order of the dominance on CTL is such that chloride binding < buffering capacity of cement matrix < physical condition of steel-concrete interface. This is attributed to the fact that calcium hydroxide does not form a continuous layer on the steel surface and that bound chlorides are released at the stage of corrosion initiation.

1. Introduction

The most important factor influencing the CTL may be the condition of the steel-concrete interface. The importance of the steel-concrete interface was postulated by Page [1] and then was first supported by an experimental work of Yonezawa et al [2]. External factors such as the humidity and temperature of concrete also influence the CTL, but it is almost impossible in practice to control such environments for the purpose of raising the CTL. The influence of cement type or cement replacement is subject to debate. There is no proof that either raises or reduces the CTL.

The present work concerns the factors of the CTL by surveying published literature and the experimental works. Apart from the environmentally external factors that are mostly impossible to control in field, the influence of chloride binding, acid neutralisation capacity (ANC), physical condition of steel-concrete interface and cement replacement were extensively investigated. To avoid unnecessary confusion which may be induced by different expressions of CTL (i.e. total chloride, free chloride or ratio of $[Cl^-]:[OH^-]$), all the CTL in this study were represented in percentage of the total chloride content to cement weight.

2. Chloride binding capacity

Binding capacity has been regarded as important in corrosion protection and CTL because of the conventional view that chemically bound chlorides do not participate in corrosion process. This postulation is supported by the poor performance of SRPC concretes compared to OPC in preventing corrosion.

The strong relationship shown between the CTL and C_3A content is supported by AC impedance and corrosion potential monitoring which found that OPC concrete with 11.2% of C_3A produced at least 1% of the CTL by weight of cement, while SRPC with 1.41% of C_3A lowered the CTL [3]. It was also observed that C_3A was more effective

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than C_4AF in binding chloride. The paper by Page et al [4] also indicated that SRPC offers the higher corrosion ratethan OPC or cement replaced with PFA and GGBS, whilst the cements containing GGBS or PFA are slightly more effective than typical OPC in the ability to protect steel from chloride-induced corrosion.However, the data from Suryavanshi et al [3] is less convincing, because the detection methods could not measure the onset of corrosion with any certainty. It is not surprising that the corrosion rate for SRPC concrete (i.e. less chloride binding) is much higher than for OPC concrete, because higher free chloride levels result in the rapid propagation of corrosion.

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 [5] shows no correlation between the CTL and chloride binding capacity. Breit and Schiessl [6] reported similar CTL values for OPC and SRPC concretes, ranging 0.2-0.4%. This suggests that chloride binding capacity has less influence on the CTL, possibly due to the participation of bound chloride in the corrosion initiation process.

At a pH of 10, most of the bound chloride ions are released as the free chlorides. However, if a large portion of bound chloride is not released even in the low pH environment of depassivation, a continued supply of chlorides is necessary to initiate corrosion, thereby increasing the CTL. This has led to the acid neutralisation capacity (ANC) concept, which is discussed in the following section (Section 3).

3. Buffering capacity

Glass et al [7] performed the ANC test on chloride contaminated concrete specimens and also measured the change in free chloride content as the pH was decreased. Fig. 1 gives the pH dependent release of chloride and ANC analysis plot. It is evident that most 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. The pH dependent solubility of chloride in concrete suggests that the buffering capacity of the cement matrix strongly affects the resistance to corrosion initiation and the CTL may be influenced by the release rate of bound chloride rather than binding capacity or C_3A content. This hypothesis is supported by the ANC of OPC, a mixture of OPC and 10% calcium aluminate cement (CAC), SRPC, 30% PFA or 65% GGBS concretes and by the present experimental work on CTL. Table 1 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 CTL can be different even for the same mix (same binding capacity and same ANC value). This may be attributed to other factors, which may include the condition of the steel-concrete interface, as discussed in Section 4.

4. Steel-concrete interface

It is well known that 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 presence of voids at the interface affects the local buffering capacity and influences the CTL. The importance of voids at the interface on the CTL is supported experimentally by Yonezawa et al [4]. However, the conclusion in this work was based on data obtained on a limited number of mortar specimens with cast-in chloride. The CTL was quantified as the [Cl⁻]:[OH⁻] ratio, which gave a very large range of values on apparently identical samples.

The importance of entrapped air voids adjacent to the embedded steel has been emphasised, because corrosion starts there. It has been currently observed that 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. It is due to

the fact that voids, in the vicinity of the steel, saturated in the pore solution provide the more active environment for electrochemical reaction (i.e. corrosion) than the cement matrix which relatively restricts current flow between anode and cathode.

As shown in Fig. 2, the experimental work using an external source of chloride and with air voids generated parallel to the casting direction, showed good correlation between the CTL and the air void content at the steel-concrete interface. An increase in the air void content to 1.0% at the interface resulted in a decrease in the CTL, but increasing the air void content did not change the CTL. This relationship was also confirmed in the present work.

Characterization of the physical condition of the steel-concrete interface is needed in order to quantify the effect of the interfacial void content on the CTL. The usefulness of a correlation between the interfacial condition and the CTL will be enhanced if a non-destructive test can be used to identify the condition of an existing interface. However, a review showed that most of the non-destructive tests used in concrete are associated with progressive damage rather than determining the presence of defects. Research is currently being undertaken at Imperial College to quantify the steel-concrete interface condition by non-destructive means.

5. Cement replacement

When cement is replaced with additional materials such as PFA or GGBS, the CTL may increase or decrease depending on the chloride source (internal or external). Thomas [8] showed that an increase in the content of PFA in concrete, which allows external chlorides to penetrate, produced a remarkable decrease in the CTL regardless of the free water-binder ratio. The resistance to corrosion measured by the mass loss of the steel embedded in concrete was decreased as the content of PFA increased. In contrast, it was reported that the CTL for PFA or GGBS concretes was higher than that for OPC, when the chloride was introduced in the mixing water.

Fig. 3 gives the CTL for PFA and GGBS concretes exposed to internal or external chlorides. The reason for the difference in the CTL between GGBS or PFA is not clear. Oh et al [9] obtained the CTL for 30% GGBS and 30% PFA concretes, ranging 0.9 and 0.97% by weight of cement respectively, while the CTL for OPC ranges 0.78, 0.93 and 0.89% with water-cement ratios of 0.35, 0.45 and 0.55 respectively. This discordance on the CTL for replacing materials may arise from other more dominant factors such as physical condition of the steel-concrete interface, roles and chemical reactions of chlorides in this cement matrix for corrosion initiation.

Notwithstanding debate over the effect of cement replacement on the CTL, PFA or GGBS concrete is beneficial in delaying the time to corrosion (external chloride source). It is well known that chloride transport is reduced in PFA and GGBS concretes due to (1) the presence of fine particles introduced by the filler (i.e. filler effect) and (2) the increased binding capacity. This is experimentally supported by reports showing that the time to corrosion is delayed by cement replacement with PFA or GGBS.

6. Conclusion

(1) 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 corrosion initiation at a lower CTL.

(2) The majority of previous studies have investigated the influence of binder type, in particular C_3A content, on the CTL. This has not resulted in a more precise definition because CTL is influenced more by the rate of release of free chloride from bound chloride caused by a local fall in the pH, often expressed as the ANC rather than binding capacity.

(3) The influence of replacing materials such as PFA or GGBS on the CTL is subjected to debate. The CTL in the use

of pozzolanic materials depends on whether chlorides introduced from an external environment or from an internal source as cement ingredients. However, their use may be advantageous because of the lower rate of chloride ingress in concrete, thereby increasing the time to corrosion.

References

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Table 1 The buffering capacity of various concretes as measured by the ANC method

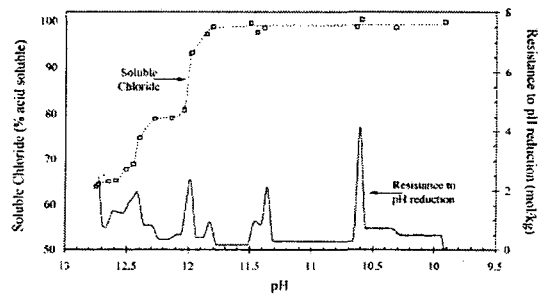| pH	ANC (mol/kg)			CTL (%, cement)
	12	11	10	
OPC	1.05	1.75	2.25	0.23-1.52
10% CAC	0.83	1.87	2.26	0.72-2.35
SRPC	0.92	1.26	2.08	0.31-0.53
30% PFA	0.51	1.23	1.8	0.25-0.35
65% GGBS	0.41	1.31	1.73	0.22-0.51

Fig. 1 pH dependent release of chloride and ANC analysis plot obtained from chloride-contaminated OPC concrete [7]
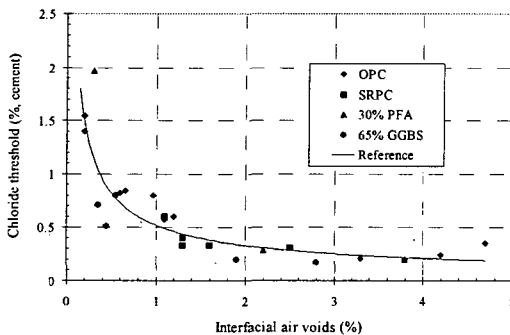

Fig. 2 Relation between the chloride threshold level and the entrapped air void content at the steel-concrete interface
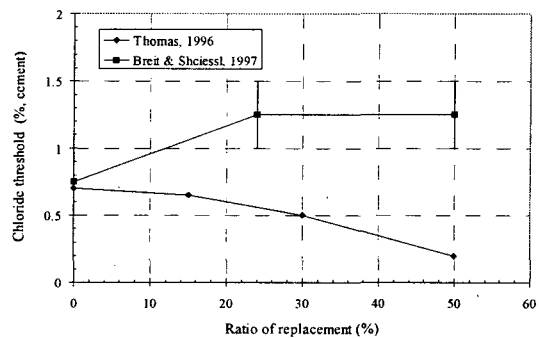

Fig. 3 CTL of PFA and GGBS concrete exposed to internal and external chloride environments